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# PHYSICAL REVIEW

## ON BILLITZER'S METHOD FOR DETERMINING ABSOLUTE POTENTIAL DIFFERENCES.

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IN an interesting article on Absolute Potential Measurements which appeared in Drude's Annalen,[1] in 1903, Mr. J. Billitzer describes three new experimental methods of determining the absolute potential between a metal and a liquid, and presents results obtained by these methods which, although sufficiently concordant among themselves, are completely at variance with those generally accepted, based upon the well-known surface tension phenomena. The magnitude of the discrepancy may be judged of by the fact that the value of the potential of a normal calomel electrode determined by the proposed methods is 0.74 volt above the value generally assumed. To explain this discrepancy the author suggests a modification of Helmholtz's double layer theory, namely that the opposed charges of a double layer are not, as heretofore assumed, equal, but that a positive or negative charge preponderates according to circumstances.

The theoretical importance of the questions thus raised by the results of this investigation seemed to us to make a further verification of the experiments on which the conclusions of the articles are based desirable. With this in view we undertook to repeat with as great care as possible the experiments described. As the exact conditions under which the experiments were carried out, particularly as regards the concentration of the solutions used, are stated

[1] Ann. der Phys , 11, 902, 937, 1903.

very vaguely by the author, it was difficult or impossible to know just what the exact conditions were. We have attempted however to reproduce them as nearly as possible. It may be stated in advance that our experiments do not furnish a satisfactory confirmation of the results in question.

## THE PROPOSED METHODS.

The line of reasoning on which the proposed methods are based may be briefly stated as follows. If a minute metallic ball or particle be suspended in a liquid between which and the particle a difference of potential exists, there is formed at the surface of contact of the two a double layer (Helmholtz). The metal may possess a positive or negative charge with respect to the liquid depending upon the electrolytic solution pressure of the metal (Nernst), and on the concentration of the ions of the metal in the solution. If such a suspended ball or particle, supposed positively charged, be placed in the path of a strong potential gradient maintained from an external source by immersing two electrodes in the liquid, the positive charge on the particle will be attracted to the negative electrode or cathode, and the negative charge of the double layer in the liquid will tend to move in the opposite direction to the positive pole or anode. A motion of the particle in the direction of the current, *i. e.*, toward the cathode should result. If the polarity of the double layer be reversed, the motion should be in the opposite direction. If the potential between particle and liquid is zero, *i. e.*, the double layer disappears, there should be no motion. Electrostatic effects arising from induction due to unsymmetrical disposition of the ball with respect to the electrodes are of course supposed to be eliminated by observing with reversals of the polarity of the electrodes producing the field. Absence of motion of a particle or minute metallic ball suspended in a liquid through which a potential drop is maintained is taken therefore as indicating zero potential between the metal in question and the liquid, and if an auxiliary electrode of the same metal as the suspended particle be immersed in the liquid the potential between it and the liquid is also assumed zero. Such an electrode can then be used as a standard of reference in combination with other electrodes to deter-

mine the absolute potential difference between them and the solution in which they are immersed respectively.

The three following methods all based on this principle are proposed. The essential difference between them is the mode of observing the reversal point or disappearance of the double layer.

1. The deflection of a minute ball fused at the end of fine wire and suspended in a liquid by a quartz fiber is noted.

2. The direction of migration of a colloidal metallic suspension is noted.

3. The potential difference produced at the ends of a tube of liquid when a metallic suspension is allowed to fall through the liquid is noted.

In the experiments described by Billitzer all three methods lead to practically the same result, namely that a reversal of motion in case 1 and 2 and reversal of potential in case 3 occurs when the potential between the auxiliary electrode in the solution under investigation and a 0.1-normal calomel standard electrode is + 0.125 volt, or in other words assuming the P.D. at the auxiliary electrode to be zero, the P.D. (solution to metal) of a 0.1-calomel electrode is + 0.125 volt, *i. e.*, 0.74 volt greater than the value — 0.614 volt usually assumed.[1]

In the present paper we have repeated the experiments made by the first method. The experiments described under the second method have at the same time been made the subject of an investigation by Dr. J. C. Blake in connection with an extended research on colloids.[2] The results obtained by him failed completely to confirm those obtained by Billitzer, for it was found that the direction of migration of the metallic colloid (Bredig) could be varied at will by the addition of a greater or less amount of gelatine which it was necessary to add to prevent coagulation of the colloid when an electrolyte was added to the solution. Billitzer also used

[1] Billitzer erroneously adopts in his computation the P.D. of a normal calomel electrode instead of that of 0.1-normal electrode which he used in his experiments, *i. e.*, he bases his potentials on the value — .277 volt (normal hydrogen electrode = 0) instead of the correct value — .337 volt. The first of these values is moreover incorrect; the value should be taken as — .283 volt. See Wilsmore, Zeit. für Phys. Chem., **36**, 91, 1901.

[2] Am. Journ. Chem. Soc., **26**, 1378.

gelatine for this purpose in all of his experiments, but he fails to state in his article exactly how much was added. In his paper "ein Spur" is stated as being sufficient, while in a letter to Blake he states that "recht viel" was added.[1] The reversals observed by Billitzer in these experiments would seem therefore to be due to the variable gelatine concentration rather than to the disappearance of the double layer on the suspended particles, and hence his conclusions relative to the potential of reversal, so far as they rest on experiments based on the second method, do not appear to be warranted.

In view of the above results and those described below, the third method has not been further investigated.

## APPARATUS AND METHOD.

The form of apparatus employed in our investigation was essentially that described by Billitzer. The following details are given for completeness and reference.

*The Suspension.* — A platinum wire 1.5 cm. long and 0.025 mm. in diameter with one end fused to a minute sphere was attached to a quartz fiber 26 cm. long by means of a bit of sealing wax. The fiber was suspended by means of a small loop of wire attached to its upper end from a hook of fine wire sealed into a glass tube. This tube could be raised or lowered through a cork which fitted the upper end of a glass guard tube to protect the fiber from air currents. The guard tube was 2.5 cm. in diameter and 35 cm. long. The lower end was drawn down and flared at the bottom as shown in Fig. 1.

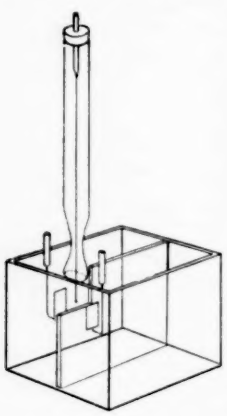

Fig. 1.

*The Electrodes.* — The electrodes to which the 110-volt or 220-volt circuit was applied to produce a potential gradient through the liquid in which the wire was suspended were of platinum foil 4 mm. × 8 mm. to which platinum wires were welded and sealed into glass tubes, contacts being made in the tube by means of mercury.

[1] Journ. Amer. Chem. Soc., **26**, 1378.

Two auxiliary platinum electrodes for measuring the potential of the liquid were used, one platinized and the other smooth. These were each 0.5 cm. × 1.0 cm.

*The Vessel.* — The vessel for containing the liquid was a cubical glass cell 5 × 5 × 5 cm. To concentrate the potential gradient at the suspended ball a glass partition was introduced as shown in Fig. 1. The opening in which the suspension hung was about 1 × 2 cm. The electrodes were placed one on each side of this partition. The whole vessel could be set into a beaker, the top of which was hermetically sealed by a paraffine cover through which the guard tube, electrodes, siphon and auxiliary tubes for withdrawing and admitting gases other than air were sealed. This permitted working in an atmosphere of hydrogen, carbon dioxide, etc.

*Mounting.* — With so delicate a suspension as that employed, the effect of mechanical jar had to be eliminated as far as possible. For this purpose the apparatus was set up on a brick and masonary pier free from the walls and floor of the building but still far from steady owing to heavy traffic in the street. On this was placed a slate block 51 × 51 × 15 cm. resting on hair felt, and on the slate block was placed a massive iron block 30 × 30 × 15 cm. The best results were obtained by supporting the iron block on three rubber stoppers placed at the vertices of an equilateral triangle. All of the apparatus was mounted on the iron block with the exception of the microscope which rested on the slate block, to permit adjustment without jarring the suspension and liquid. Even with this arrangement occasional vibrations were noticeable, but these were so small as not seriously to interfere with the observations.

*Potential Measuring Apparatus.* — For measuring the potential of the auxiliary electrodes against a 0.1-normal calomel electrode, the usual Poggendorff compensation method was used with a Lippmann electrometer sensitive to 0.001 volt as indicating instrument. The bridge constant was determined before each set of measurements by means of a Weston cadmium cell whose electromotive force determined against the laboratory standard Clark cell was found to be 1.020 volts.

The liquid in the cubical-shaped cell described above was connected with a 0.1-normal calomel electrode through an intermediate

vessel containing 0.1-normal potassium chloride. Connection was made by means of a siphon containing 0.1-normal potassium chloride

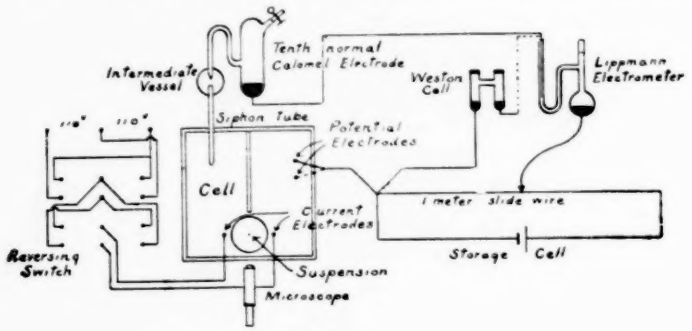


Fig. 2.

solution gelatinized by a little agar-agar. The complete arrangement of the apparatus is shown in Fig. 2.

## EXPERIMENTAL RESULTS.

We first made a number of preliminary qualitative experiments with the substances examined by Billitzer. The results agreed in the main with his, although there were several notable exceptions as will be seen from Table I.

TABLE I.

*Qualitative Experiments.*

| Substance. | Billitzer. Charge of Pt. vs. Solution. | Goodwin & Sosman. Charge of Pt. vs. Solution. | Remarks. |
|---|---|---|---|
| Air. | — | — | |
| Distilled water. | — | — | |
| Water + trace NaCl. | — | — | KCl added instead of NaCl. |
| " + " acid. | — | — | HCl added. |
| " + Br. | — | — | |
| Acetone. | — | + | |
| Ethyl alcohol. | + | — | No deflection observed at first. |
| Formaldehyde. | + | + | |
| Hydrogen peroxide (40 per cent.). | + | — | 2 per cent. was found to evolve too much gas for observation. |
| Ether. | + | + | |
| Chloroform. | + | + | No deflection at first. |

A disagreement between our results and Billitzer's, which numerous repetitions of the experiment failed to remove, was found in

the sign of the deflections in the case of acetone, ethyl alcohol and hydrogen peroxide. We were first inclined to attribute the disagreement to possible differences or impurities in the solutions, and proceeded at once to quantitative measurements in which the concentrations of our solutions were definitely known.

The first solutions thus investigated were mixtures of alcohol and water as the concentrations used by Billitzer were definitely stated for this particular case, and an exact repetition of the experiments seemed possible. The solutions used in our experiments were made up from 96 per cent. alcohol, while Billitzer states 94 per cent. as the strength used by him. Three concentrations were studied, 96, 81 and 32 per cent. respectively, thus covering the extreme range of concentrations previously investigated. Our results together with the corresponding ones obtained by Billitzer are given in Table II. In this and the following tables a negative deflection signifies that the motion was towards the anode, *i. e.*, the suspended wire was negatively charged with respect to the solution. The "deflections" are expressed in arbitrary divisions of the filar micrometer, their sign only being significant.

TABLE II.

*Alcoholic-Aqueous Solutions.*

| Goodwin & Sosman. | | | | | | Billitzer. | | |
|---|---|---|---|---|---|---|---|---|
| Per Cent. Concentration. | E. M. F. | Deflection. | Platinized Pt. vs. 0.1 Normal Electrode. | Polished Pt. vs. 0.1 Normal Electrode. | Fine Pt. Wire vs. 0.1 Normal Electrode. | Per Cent. Concentration. | Platinized Electrodes vs. 0.1 Normal Electrode. | Deflection. |
| 96 | 220 | −2 to −3. | +0.050 | | +0.07 | 94 | +0.155 | + |
| 96 | 220 | −1.0 | +0.003 | +0.15 | | 85 | +0.15 | + |
| 81 | 220 | −0.3 to −1.0 | +0.037 | | +0.12 | 70 | ? | ? |
| 32 | 220 | −3.5 to −4.0 | +0.086 | +0.10 | +0.14 | 31 | +0.139 | − |

The observations were taken after the lapse of one half hour to an hour to allow an equilibrium condition to be established between electrodes and solution. The variable values of the "deflection" are the result of a new vertical or lateral adjustment of the position of the suspended wire between the polarizing electrodes. It is to be noted that no positive deflection could be obtained even in 96

per cent. alcohol although Billitzer's results showed such deflections to occur in 78 per cent. alcohol and even 70 per cent. solutions. Moreover the potentials of the three types of auxiliary electrodes used, namely, platinized platinum, smooth platinum and wire similar to the suspended wire, showed no satisfactory agreement either with Billitzer's corresponding values or with each other. Results obtained with the platinum wire agreed on the whole best with Billitzer's. As to the best form of auxiliary electrode to use and the probable cause of the above discrepancies reference will be made later.

The power which alcohol possesses of reversing the potential of a platinum electrode as observed by Billitzer, is explained by an auto-oxidation by which hydrogen peroxide is formed. Hence it was concluded that addition of small amounts of this latter substance should also have the power of reversing the potential of platinum in acid solution. This prediction was borne out by Billitzer's results, a reversal occurring as before at approximately 0.125 volt, *i. e.*, platinized platinum *vs.* 0.1-normal calomel electrode. We repeated these experiments varying the concentration of hydrogen peroxide from 0.2 per cent. to 0.001 per cent., but obtained in every case a negative deflection. The condition of our solutions must have been essentially the same as Billitzer's, as the potential of the platinized electrode *vs.* 0.1-normal calomel electrode agreed fairly well with that found by him. It may be noted here that hydrogen peroxide was one of the substances which in our preliminary experiments was found to give results disagreeing with the published ones. Billitzer obtained a positive deflection in 40 per cent. hydrogen peroxide. We were unable, however, to obtain reliable deflections with even a 2 per cent. solution on account of the violent disturbances in the liquid arising from the decomposition of hydrogen peroxide in the presence of platinum. Our results are given in Table III. together with Billitzer's first series with hydrogen peroxide for comparison. The concentrations in his experiments were not stated.

As an example of a strong reducting agent capable of effecting a potential reversal, formaldehyde was found by Billitzer to reverse the deflection when the platinum potential *vs.* 0.1 normal calomel electrode was as before 0.125 volt. As no statement is given to in-

TABLE III.

*Hydrogen-peroxide Solutions.*

| Goodwin & Sosman. | | | | | Billitzer. | |
|---|---|---|---|---|---|---|
| Concentration in Per Cent. | E.M.F. | Deflection. | Platinized Pt. vs. 0.1-Normal Calomel Electrode. | Smooth Pt. vs. 0.1-Normal Calomel Electrode. | Deflection. | Platinized Pt. vs. 0.1 Normal Electrode. |
| 0.2 | 220 | −1.0 to −1.5 | +0.29 | | + | +0.4 |
| 0.1 | 220 | −5.0 to −6.0 | +0.28 | +0.28 | + | +0.3 |
| 0.02 | 220 | −6.0 | +0.23 | | + | +0.2 |
| 0.004 | 110 | −2.5 | +0.20 | | + | +0.15 |
| 0.001 | 220 | −3.5 | +0.19 | +0.20 | ? | +0.12 |
| | | | | | — | +0.10 |
| | | | | | — | +0.08 |

dicate whether weak or strong solutions of the substance were used we extended a series of measurements from a 40 per cent. to a 0.04 per cent. solution. In this case we were able to detect a reversal in the deflection in passing from a 10 per cent. to a 36 per cent. solution. The reversal potential however did not check Billitzer's, as will be seen from the results given in Table IV.

TABLE IV.

*Formaldehyde Solutions.*

| Goodwin & Sosman. | | | | | Billitzer. | |
|---|---|---|---|---|---|---|
| Concentration in Per Cent. | E. M. F. | Deflection. | Platinized Pt. vs. 0.1-Calomel Electrode. | Smooth Pt. vs. 0.1-Calomel Electrode. | Deflection. | Platinized Pt. vs. 0.1-Normal Electrode. |
| 40 | 220 | 0 to +0.3 | −0.02 | +0.06 | + | +0.17 |
| 36 | 220 | +0.3 | −0.03 | +0.04 | + | +0.15 |
| 36 | 220 | +0.2 | +0.02 | +0.07 | + | +0.14 |
| 10 | 110 | −1.5 to −2.0 | −0.04 | | + (?) | +0.13 |
| 10 | 220 | −2.5 | −0.04 | | — | +0.12 |
| 2 | 220 | −2 | −0.06 | +0.06 | — | +0.11 |
| 0.4 | 110 | −1.5 to −2 | −0.10 | +0.01 | — | +0.10 |
| 0.2 | 110 | −1.0 to −1.5 | −0.07 | +0.03 | — | +0.09 |
| 0.08 | 110 | −2.0 | +0.02 | +0.04 | | |
| 0.04 | 110 | −4. to −5. | +0.01 | +0.07 | | |

Finally we repeated the series of experiments in which the variation of the reduction potential of a solution was varied between wide limits by changing the relative concentration of ferrous and

ferric ions in the solution. Billitzer found that by varying the relative concentration of these ions a reversal of the deflection of his test electrode occurred again at the characteristic potential between 0.10 and 0.13 volt. We did our best to check these results but without success. Our only guide for duplicating the concentration used was the statement that "die Koncentration der ursprünglichen Lösung wurde in verschiedenen Fällen verschieden, immer jedoch sehr klein gewählt." Billitzer used ferrous and ferric sulphates in his experiments; we used ferric chloride and ferrous sulphate.

TABLE V.

*Ferrous and Ferric Salt Solutions.* ($Fe_2Cl + FeSO_4$) *in Various Proportions.*

| Goodwin & Sosman. | | | | | | Billitzer. | |
|---|---|---|---|---|---|---|---|
| Concentration in Per Cent. | | E.M.F. | Deflection. | Platinized Pt. vs. 0.1-Calomel Electrode. | Smooth Pt. vs. 0.1-Calomel Electrode. | Deflection. | Platinized Pt. vs. 0.1-Normal Calomel Electrode. |
| $FeCl_3$. | $FeSO_4$. | | | | | | |
| 0.001 | 0 | 220 | 0 | +0.36 | +0.41 | + | +0.16 |
| | | 110 | −1.5 | | | + | +0.15 |
| | | 220 | −3.0 | | | + | +0.14 |
| 0.001 | 0.02 | 220 | −2.5 | +0.32 | | + | +0.13 |
| 0.001 | 0.03 | 220 | −1.0 | +0.315 | | (very weak.) | +0.125 |
| 0.001 | 0.05 | 220 | uncertain because of electrolysis. | +0.23 | | — | +0.10 |
| | | | | | | — | +0.09 |
| 0.05 | 0 | 220 | uncertain because of electrolysis. | +0.50 | +0.46 | | |
| 0.035 | 0 | 220 | uncertain because of electrolysis. | +0.49 | | | |
| 0.035 | 0 | 220 | uncertain because of electrolysis. | +0.43 | | | |
| 0.001 | 0 | 220 | negative | +0.38 | +0.29 | | |
| 0 | 0.1 | 220 | electrolysis. | +0.27 | +0.25 | | |

In these experiments reliable deflections could be obtained only in the very dilute solutions on account of electrolysis. Whether the solution contained ferrous or ferric ions the platinum suspension showed deflections indicating the metal to be negatively charged in all cases. The auxiliary platinum electrode was under the same conditions always positively charged referred to Ostwald's zero.

### Mercury and Silver Electrodes.

In the above experiments platinum is to be regarded as an oxidation or reduction electrode. Among other metals whose electrolytic solution pressure is such that a reversal of their potential with respect to a solution can be effected by varying the ionic concentration of the solution, may be mentioned mercury and silver. These metals were both tried by Billitzer, the former as amalgamated fine platinum wire, and the latter in the form of very fine silver wire. Auxiliary electrodes of the pure metals were used for measuring the potential of the solutions against a 0.1-normal calomel electrode as before.

We tried both of these metals but obtained a reversal only with mercury. A reversal was observed by Billitzer with mercury in mercuric nitrate, in one experiment only.

In these experiments the suspended platinum wire ball was amalgamated by being placed as cathode in a solution of mercuric nitrate acidulated with nitric acid. The auxiliary potential electrode of platinum was similarly amalgamated. After amalgamation the wire showed numerous swellings along its length about 0.04 mm. in diameter, the wire being 0.025 mm. in diameter. The strongest mercuric nitrate solution used in the following measurements was 2.5 per cent. acidulated with six drops of nitric acid in 200 c.c. A solution of 0.1-normal potassium nitrate was used in the siphon to connect with the calomel electrode. The results are given in Table VI.

Table VI.

*Mercury in mercuric nitrate solutions.*

| Concentration in Per Cent. | E.M.F. | Deflection. | Amalgamated Pt. vs. 0.1-Normal Calomel Electrode | Remarks. |
|---|---|---|---|---|
| 2.5 | 110 | +1.5 to +4 | +0.405 | No deflection at first. |
| 1.25 | 110 | +2.5 | +0.403 | " " " |
| 0.13 | 110 | +0.3 to +0.4 | +0.385 | |
| 0.025 | 110 | −0.4 | +0.364 | |
| | 220 | −0.4 | | |
| 0.013 | 220 | −1.5 | +0.350 | |

It is to be noted that the reversal potential (between + 0.36 and + 0.39 volt) does not agree with Billitzer's + 0.125 value.

In the case of silver Billitzer could get no reversal by diluting a silver nitrate solution. The reversals all indicated the silver was positively charged *vs.* the solution. By the addition of potassium cyanide the concentration of silver ions can be almost indefinitely diminished and it is well known that the metal becomes negatively charged with respect to such a solution. Billitzer observed by his second method (direction of migration of colloids) that addition of potassium cyanide produced a reversal when the auxiliary electrode indicated a potential of between + 0.11 and + 0.16 volts *vs.* 0.1-normal electrode. We tried the experiment of noting the deflection of a very fine silver wire 0.043 mm. diameter suspended as before by a quartz fiber in an excessively dilute silver nitrate solution to which potassium cyanide was added. No trustworthy observations could be obtained at concentrations greater than about 0.0005 normal on account of electrolysis. As will be seen in Table VII., deflections were always negative even when the auxiliary silver electrode changed in potential from + 0.27 volt to − 0.30 volt *vs.* the 0.1-normal calomel standard. In silver nitrate alone we have certainly every reason to regard silver as positive *vs.* the solution, yet the sign of the deflections observed, if they are determined by the charge alone, would indicate the contrary.

TABLE VII.

*Silver in silver nitrate + potassium cyanide.*

| Concentration in Mols. $AgNO_3$. | E.M.F. | Deflection. | Ag. Electrode vs. 0.1-Normal Calomel. | Remarks. |
|---|---|---|---|---|
| 0.01 | 110 | uncertain | +0.35 | Electrolysis. |
| 0.005 | 110 | " | +0.33 | " |
| 0.0005 | 110 | −1 | +0.27 | |
| | 220 | −1.5+ | +0.27 | |
| 0.0001 | 220 | −0.5 | −0.30 | .01-Normal $AgNO_3$ ppt. and redissolved in KCN and diluted ten times. |

DISCUSSION.

A consideration of the preceding results show that:

*First:* The phenomenon in question, *i. e.*, of the reversal in deflection of the suspended wire does not appear to be general, but

occurs only in exceptional cases. The general phenomenon would seem to be a motion of the suspended metal towards the *anode*.

*Second:* The reversal phenomenon does not appear to stand in any definite relation to the potential between the auxiliary electrode and the solution, the characteristic reversal potential of + 0.125 volt (platinum *vs.* 0.1-normal calomel electrode) found by Billitzer being in no case observed.

These two experimental facts seem to us to be reasonably well established by our experiments. We do not attempt to offer an explanation for the remarkably concordant results of Billitzer leading to entirely contrary conclusions. It is possible that some essential condition was observed in his work not sufficiently stated in his article to enable us to duplicate it in our experiment. If so we trust that it will be more clearly pointed out. Attention may be called, however, to several factors which impressed themselves upon us in the course of our work, which have a direct bearing on the phenomenon under discussion and which may lie at the foundation of the results observed.

### Effect of Electrode Surface.

Does the auxiliary electrode indicate the same potential as that existing between the fine suspended wire and the same liquid? This is evidently a fundamental question as the interpretation of all results obtained by Billitzer rests on the assumption that the two are identical.

We carried out several experiments to test this point by comparing against a 0.1-normal calomel electrode the potential drop between a platinized electrode, a polished electrode and an electrode consisting of a fine wire used for the suspension. It might be expected that since the last is smooth wire with a ball fused at the end, it would comport itself electrometrically more nearly like the polished platinum electrode than the platinized electrode. It was found that potential measurements with such extremely fine wire electrodes and even with electrodes consisting of a bunch of such wires were difficult to make and rather uncertain in their results. The following figures show that the potential of a fine wire electrode and a platinized electrode in the same liquid may differ by several hundredths of a volt, the former being always higher.

| Solution. | Wire. | Platinized. | Polished. |
|---|---|---|---|
| Formaldehyde. | +0.02 | −0.064 | +0.059 |
| " | +0.10 | +0.019 | +0.041 |
| Alcohol-water. | +0.07 | +0.050 | |
| " | +0.12 | +0.037 | |
| " | +0.14 | +0.086 | +0.100 |

Polished electrodes were found to be far less certain in their behavior than platinized electrodes, as was to be expected, and it might be fairly assumed that the wire electrodes would show similar irregularities. Platinized electrodes, on the other hand, when properly prepared by treating as cathode in dilute sulphuric acid to reduce and remove residues of the platinizing liquid (Ostwald), then washed in boiling water, gently heated and finally allowed to stand in distilled water, always gave concordant results among themselves.

*Effect of Time on Potential Equilibrium.* — A very marked effect of time on the potential of the auxiliary electrode was noted in some cases which was different for platinized and unplatinized electrodes. This was most marked in the case of formaldehyde solutions, and was noticeable in all other solutions except those of hydrogen peroxide and mercuric nitrate.

A gradual change in the solution may account in part for the progressive rise in potential observed: the point we wish to make however is, that the time required to reach equilibrium was much greater in the case of the platinized than in the case of the unplatinized electrode, and if the unplatinized suspended wire comports itself like the polished potential electrode the same kind of uncertainty in its indications as to deflections would result.

The cause of the gradual rise of potential of the auxiliary electrode potential, observed in distilled water was also investigated. The potential was lower in freshly boiled water than in water which had stood some time in air: the effect was therefore ascribed at first to dissolved oxygen, but when pure air was passed through carefully boiled water to resaturate it, the potential fell instead of rising. This suggested at once that carbon dioxide caused the change. Carbon dioxide from the lungs was passed through the water, and the potential rose; this carbon dioxide was then washed out by a current of pure air, and the potential fell to the value first obtained in

air-washed water. Saturation of the water with pure carbon dioxide brought the potential up somewhat above that obtained in water which had stood in contact with air. Tory and Barnes[1] have observed such an effect with platinum, and ascribed it to air; it may be possible to explain their results by the presence of carbon dioxide.

*Effect of Liquid Junction.* — Of minor importance in the present investigation is the value of the potential difference arising at the junction of the 0.1-normal electrode and liquid under investigation. This is at best uncertain in experiments like the above, and although in many cases it is probably small owing to the nearly equal migration velocities of potassium and chlorine ions, yet with the somewhat complicated nature of the solutions and solvents used and their extreme dilution it is possible that it may attain a very appreciable value.

EFFECT OF DISSOLVED GASES ON THE SIGN OF THE DEFLECTION.

We would like to point out one other factor which seems to us of much greater importance on the phenomenon in question than any of the preceding, and one which apparently has not been considered by Billitzer. We refer to the phenomenon described and investigated in 1861 by Quincke,[2] who found that minute bubbles of hydrogen, oxygen and air act exactly like solid particles when suspended in a liquid and *migrated towards the anode* when a current was passed through an aqueous solution containing them. In turpentine, however, he found that all substances which he investigated (except sulphur) migrated *positively*, *i. e.*, towards the cathode. Now it was frequently observed in our experiments that no deflection was produced at the first instant the voltage was applied. After visible electrolysis had taken place and minute bubbles appeared in the liquid, a deflection of the wire became evident and the deflection was always towards the anode. This seems to us significant, for although it is true that deflections were repeatedly observed at the instant the current was established and when no bubbles were visible on the end of the suspended wire, yet is quite conceivable, and indeed probable, that in the process of immersing the wire in the

[1] Trans. Amer. Electrochem. Soc., 3, 95, 1905.

[2] Pogg. Ann., 113, 565, 1861.

liquid from the air, very minute particles of air might remain attached to it, or might separate out on it from the liquid. The following experiment in the light of Quincke's results seem to bear out the above hypothesis. The platinum wire was suspended in turpentine and deflections observed with 220 volts applied. They were unmistakably positive. The resistance of the cell was so high that the current was less than 0.00001 ampere. In distilled water saturated with pure hydrogen, the deflection was distinctly negative. The presence of minute, even invisible, bubbles of gas on the suspended electrode which may arise from gases in the solution, from the air or from electrolysis, seems therefore to offer a very plausible explanation of the results observed.

Another factor which may also have at least a secondary influence on the deflections, is the possible motion of the liquid surface under the action of the applied voltage.[1] Such a motion of the surface was frequently noticed on closing the circuit, when the microscope happened to be focused so that the surface was in the field of view. Since a difference of potential exists between a liquid surface and the gas above it, such a motion does not seem *a priori* unlikely. This phenomenon is worthy of further investigation.

## CONCLUSION.

The present investigation was undertaken in order to obtain a confirmation of Billitzer's results on absolute potentials by the method of deflections of a minute metallic electrode suspended in various solutions, under the influence of an electric current. The results obtained have failed completely to confirm the measurements obtained by him, and we are forced to the conclusion that the method proposed is not to be relied upon for the purpose for which it was developed. This conclusion is further strengthened by the results obtained by Blake on the migration of colloids, who has also failed to confirm Billitzer's measurements using the colloid method.

So far as our experiments go, it would seem that most of the phenomena observed may be explained on the assumption of the negative migration of gaseous particles in the liquid, as first demonstrated by Quincke in 1861.

[1] F. B. Kendrick, Zeitschr. f. Physikal. Chem., **19**, 625, 1896.

We believe therefore that the results obtained by Billitzer by the above described method afford as yet no sufficient grounds for rejecting the generally adopted values for the potential of the normal (or tenth normal) calomel electrode.

Since the above work was completed two other articles[1] have appeared by the same author in which he has determined absolute potentials by investigating the phenomena of concentration changes produced by the dropping electrodes first studied by Palmaer, and by a modification of Pellat's surface tension method. As the results obtained by both of these methods confirm approximately the author's previous results, a description of the precise conditions under which the former experiments were carried out seems all the more desirable.

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# ON THE DISTRIBUTION OF ENERGY IN THE VISIBLE SPECTRUM.

By Edward L. Nichols.

THE direct determination of the distribution of energy in the visible spectrum of incandescent bodies is a somewhat difficult matter. Even with the most sensitive forms of linear bolometer or with the radiometer the deflections obtained by exploring the spectrum of artificial light sources are very small excepting in the red. The proper correction of this portion of the observed curve for slit width is likewise a matter of some uncertainty. The visible spectrum of sunlight, it is true, is of sufficient strength to admit of direct measurement and the spectrum of the electric arc affords easily measurable intensities; but the distribution of energy in the former is so seriously affected by varying atmospheric absorption as to render the sun worthless as a source of comparison in spectrophotometric work and the fluctuations in the brightness of the arc are also very great.

It is possible with an exceedingly sensitive radiometer to explore the visible spectrum of an artificial source of light such as the acetylene flame up to about .45 $\mu$ and I have been in possession for some time of a collection of data for this source of light obtained from measurements by G. W. Stewart and by Mr. W. W. Coblentz. Given such a curve, one can compute the curves of distribution for all spectra which have been compared with the acetylene flame by means of the spectrophotometer; but I have hitherto postponed these computations through a feeling of distrust in the accuracy of the corrections for slit width.

Knut Ångström,[1] in a recent paper, has published a curve of the distribution of intensities in the visible spectrum of the Hefner lamp. Ångström's values were obtained by an indirect method based upon Wien's equation

[1] Ångström, Physical Review, Vol. XVII., p. 302; also Royal Society, Upsala 3d series, Vol. XX., 1904.

$$I_\lambda = C_1 \lambda^{-5} e^{-\frac{C_2}{\lambda T}}$$

In his measurements he avoids the difficulty arising from the very feeble intensities of the visible spectrum of this source of light by measuring the quantity

$$L_\lambda = \int_0^\lambda I_\lambda d\lambda = C_1 \int_0^\lambda \lambda^{-5} e^{-\frac{C_2}{\lambda T}}$$

where $L_\lambda$ is the entire radiation lying between o and $\lambda$. The constants $C_1$ and $C_2/T$ were determined by a series of such measurements and the value of the intensity of each wave length of the spectrum was then computed.

If we know the relative intensities of the spectra of the Hefner lamp and of the acetylene flame, and these are readily obtained by means of the spectrophotometer, the curve for the distribution of intensities of the acetylene flame may be deduced from Ångström's values for the Hefner lamp. I have recently shown [1] that the curve thus obtained is essentially identical with that obtained by the direct exploration of the spectrum of the latter source, to which reference has already been made.

The agreement of these results greatly strengthens our confidence in the validity of both and renders it desirable to compute the corresponding curves for the numerous sources of light of which we already possess spectrophotometric comparisons either with the Hefner lamp or with the acetylene flame. Materials for such computations are sufficiently abundant. We have, for example, the series of spectrophotometric comparisons of the Hefner flame with petroleum flames, gas flames, the light of the Welsbach mantel, the zircon light, daylight and sunlight made by Koettgen [2] and numerous similar comparisons of light sources with the acetylene flame, made from time to time in the Physical Laboratory of Cornell University. It is with the results of computations made upon such data that the present paper deals.

Ångström, in the paper already cited, determined by means of his compensated pyrheliometer the heat in calories per second

[1] Nichols' Standards of Light, Proc. of International Elec. Congress of St. Louis, 1904

[2] Koettgen, Wied. Ann., 53, p. 793.

received by a surface of 1 sq. cm. at meters distance from the Hefner flame. If the various curves for the distribution of energy in the visible spectrum of light sources are plotted to the same scale as

TABLE I.

*Distribution of intensities in spectra of Hefner and $C_2H_2$ flames.*

| Wave-lengths. | Hefner. Intensities from Ångström's Curve. | Acetylene. Intensity by Radiometer. | Wave-lengths. | Hefner. Intensities from Ångström's Curve. | Acetylene. Intensity by Radiometer. |
|---|---|---|---|---|---|
| .46 | 0.22 | 0.39 | .62 | 5.40 | 4.86 |
| .48 | 0.47 | 0.65 | .64 | 7.00 | 5.88 |
| .50 | 0.82 | 0.88 | .66 | 8.60 | 6.61 |
| .52 | 1.20 | 1.33 | .68 | 10.55 | 8.10 |
| .54 | 1.65 | 1.80 | .70 | 12.60 | 9.65 |
| .56 | 2.26 | 2.42 | .72 | 15.10 | 11.40 |
| .58 | 3.30 | 3.08 | .74 | 17.80 | 12.90 |
| .60 | 4.20 | 3.97 | | | |

Ångström's curve for the Hefner flame, with ordinates so chosen as to represent in each case a source of unit intensity, the areas of these curves would give the luminous energy received from each source in unit time per square centimeter of surface when the illumination is one lux. It was shown many years ago by Crova that the intensity of the yellow of the spectrum is proportional to the candle power of the source. This relation, which one would expect to find approximately true on account of the high luminosity of that portion of the spectrum, one can readily verify by means of the spectrophotometer. I have accordingly reduced the various curves to be considered to this unit intensity by making the ordinate for wave-length .590 $\mu$ equal in every case to that of Ång-

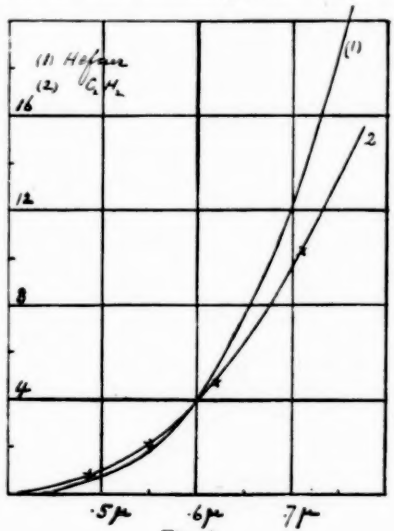

Fig. 1.

ström's curve for the Hefner flame. Ångström's curve and the corresponding curve for the acetylene flame, which are the reference curves for the reduction of the spectrometric data to be employed, are shown in Fig. 1 and the numerical data are given in Table I. Curve 2 in that figure is from direct determinations of the visible spectrum of the acetylene flame made with the radiometer, while the crosses (×) show the values for four wave-lengths computed from a spectrophotometric comparision of the acetylene and Hefner flames reduced by means of Ångström's curve for the latter.

### GAS AND PETROLEUM FLAMES.

In spite of the fact that the ordinary gas flame is somewhat indefinite, as regards the character of its spectrum, owing to the variations in the character of the fuel consumed and the temperature of combustion with different burners, it is of interest to determine the general character of such flames since these have frequently been employed as sources for spectrophotometric comparisons. Koettgen in the article already referred to has measured the spectrum of ten gas flames with reference to the Hefner lamp. The

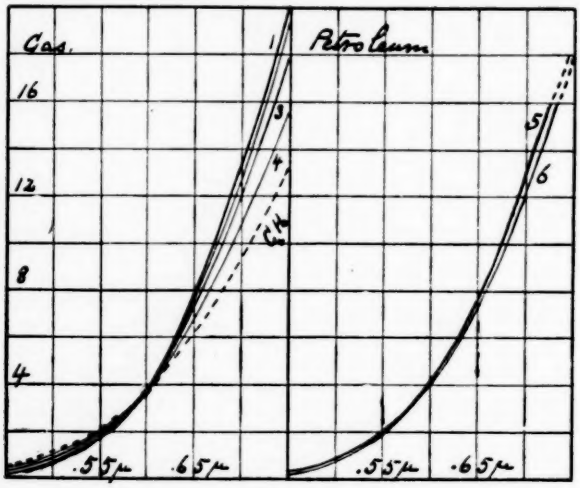


Fig. 2.

distribution in the energy of three of these, described as the *Triplex lamp, Siemen's precision burner* (*No. 1*) and *Sugg's burner*, have been computed by means of Ångström's curve. The results are given

in Table II. together with the corresponding data for an ordinary "bats-wing" burner the relation of which to the acetylene spectrum was known. The results are plotted in Fig. 2 in which the corresponding curve for acetylene is shown in broken line for purposes of comparison. The ordinates of these curves are all the same for wave-length .590 $\mu$ and are equal to that of Ångström's curve for the Hefner flame. The curve for the triplex burner (1) is almost identical throughout with the curve for the Hefner lamp. The others lie between it and the acetylene curve. These curves, and the same is true of the other curves in the present paper, give the actual distribution of intensities in the visible spectra of the sources to which they pertain and their areas are proportional to the light-giving energy. The question of the energy of visible radiation from the various sources of light to be considered is discussed in a subsequent paragraph.

TABLE II.

*Distribution of Intensities in the Spectra of Ordinary Gas Flames.*

| Wave-Lengths. | From Comparisons with Hefner Flame (Koettgen's Data). | | | From Comparison with Acetylene Flame. | |
|---|---|---|---|---|---|
| | Triplex Burner. | Siemens No. 1. | Sugg's Burner. | Wave-lengths. | Bat's Wing Burner. |
| .45 $\mu$ | 0.19 | 0.22 | 0.27 | .45 $\mu$ | 0.11 |
| .49 | 0.63 | 0.70 | 0.81 | .50 | 0.52 |
| .51 | .98 | 1.07 | 1.17 | .55 | 1.76 |
| ·55 | 1.92 | 2.00 | 2.07 | .60 | 4.40 |
| .59 | 3.50 | 3.50 | 3.50 | .65 | 7.70 |
| .61 | 4.80 | 4.69 | 4.63 | .70 | 12.70 |
| .65 | 8.01 | 7.34 | 7.04 | | |
| .69 | 12.48 | 10.8 | 10.0 | | |

Koettgen has also compared the flames of seven petroleum lamps with the Hefner flame. One of these, the flame of an ordinary lamp with a flat wick (curve 5, Fig. 2) is of greater importance than the others since it is of a type that has been used in a number of spectrophotometric comparisons. Its spectrum corresponds very closely with the Hefner and with the triplex gas burner. Six of the seven lamps investigated by Koettgen would have intensity curves lying between those of the triplex burner and of the Siemen's precision burner, curve 3, Fig. 2. Only one of the entire set of petroleum flames given in Koettgen's table lies outside these

limits and this one, the flame from the lamp known as the *Triumph patent* (curve 6, Fig. 2) differs but slightly from the Siemen's gas burner in its distribution of intensities. Curves 5 and 6 may be taken as representing the extremes of variation in ordinary petroleum flames, the range of which appears to be much smaller than that of gas flames.

TABLE III.

*Distributions of intensities in the spectra of petroleum flames, from comparisons with the Hefner flame (Koettgen's data).*

| Wave-Lengths. | Flat Burner. | Triumph Burner. |
|---|---|---|
| .45 | 0.22 | 0.23 |
| .49 | 0.81 | |
| .51 | 0.99 | 1.11 |
| .55 | 1.94 | 2.03 |
| .59 | 3.50 | |
| .61 | 4.76 | 4.73 |
| .65 | 7.42 | 7.36 |
| .69 | 11.50 | 11.40 |

INCANDESCENT CARBON.

The spectrophotometric data available for the computation of energy in the visible spectrum of incandescent carbon is contained chiefly in my articles on the visible radiation from carbon[1] and in Blaker's[2] spectrophotometric comparisons of the light from the filament of incandescent lamps. The former of these investigations consisted in spectrophotometric comparisons of the light from untreated carbon rods at temperatures between 1273° abs. and 1673° abs., with that of an acetylene flame. The relative measurements of different wave-lengths have been reduced to absolute intensities by the use of the curve for the acetylene flame in Fig. 1, and the results are given in Table IV. which shows the distribution of intensities for various parts of the spectrum in the case of a carbon rod heated successively to 1273°, 1373°, 1473°, 1573° and 1673° of the absolute scale.

These values for the three temperatures 1273°, 1573° and 1673° abs., reduced to a common ordinate in the yellow for comparison

[1] Nichols, PHYSICAL REVIEW, Vol. XIII., p. 65; Proc. of the American Academy of Arts and Sciences, Vol. XXXVII., p. 73.

[2] Blaker, PHYSICAL REVIEW, Vol. XIII., p. 345.

TABLE IV.

*Intensity of the spectrum of an untreated carbon rod at various temperatures of the absolute scale.*

| Wave-Lengths. | Intensities (Absolute). | | | | |
|---|---|---|---|---|---|
| | 1273° | 1373° | 1473° | 1573° | 1673° |
| .45 | 0.054 | 0.121 | 0.320 | 0.62 | 4.32 |
| .50 | 0.220 | 0.642 | 1.93 | 3.60 | 19.5 |
| .55 | 0.815 | 2.99 | 7.94 | 16.51 | 63.7 |
| .60 | 2.00 | 9.01 | 23.9 | 55.58 | 168.7 |
| .65 | 6.93 | 28.0 | 63.0 | 141.1 | 315.0 |
| .70 | 21.2 | 70.4 | 162.1 | 289.5 | 530.7 |
| .75 | 52.1 | 174.0 | 352.0 | 578.1 | 883.6 |

with other sources, are given in Table V. They correspond, approximately at least, to those which would be found for carbon rods having the temperatures in question but of such a size as to possess in every case the same illuminating power as the Hefner lamp.

TABLE V.

*Untreated Carbon.—Continued.*

| Wave-Lengths. | Intensities (Reduced). | | |
|---|---|---|---|
| | 1273°. | 1573°. | 1673°. |
| .45 | — | 0.08 | 0.16 |
| .50 | 0.20 | 0.26 | 0.44 |
| .55 | 1.20 | 1.40 | 1.58 |
| .60 | 4.21 | 4.08 | 4.01 |
| .65 | 13.9 | 10.30 | 7.56 |
| .70 | 42.5 | 21.1 | 12.73 |
| .75 | 104.0 | 42.2 | 21.20 |

The reduced intensities for these three temperatures are likewise shown graphically in Fig. 3. The unreduced intensities are so great, especially in the red, that they cannot be represented upon the same scale with the other curves in a diagram of reasonable dimensions. The general trend of the curves and their close similarity in character to those obtained with gas and oil flames will be evident from the figure.

Ångström, in the paper already cited, gives a curve for the distribution of intensities in the visible spectrum of an incandescent lamp the filament of which, measured by his method, had a temperature of 2000° abs. This curve reduced to correspond at wave-

length .590 $\mu$ with the curve for the Hefner flame, is likewise given for the sake of comparison in Fig. 3.

In the course of my investigation of the visible radiation from carbon, just cited, observations were made on carbon rods previously treated by flashing in an atmosphere containing hydrocarbon vapors. The surface of the rods was thus coated with a deposit of the well

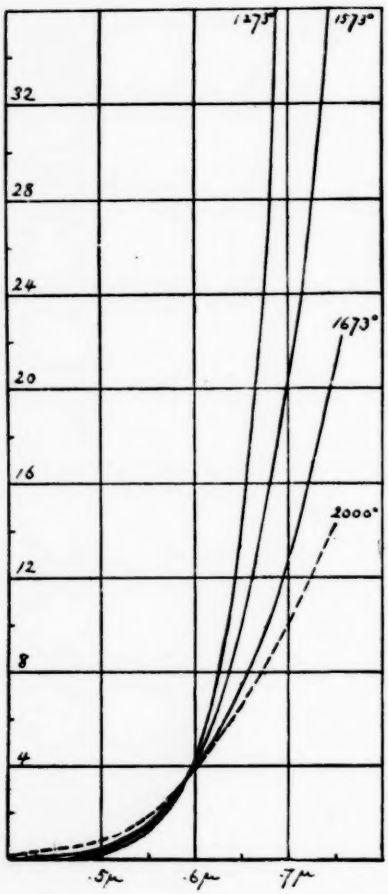

Fig. 3.

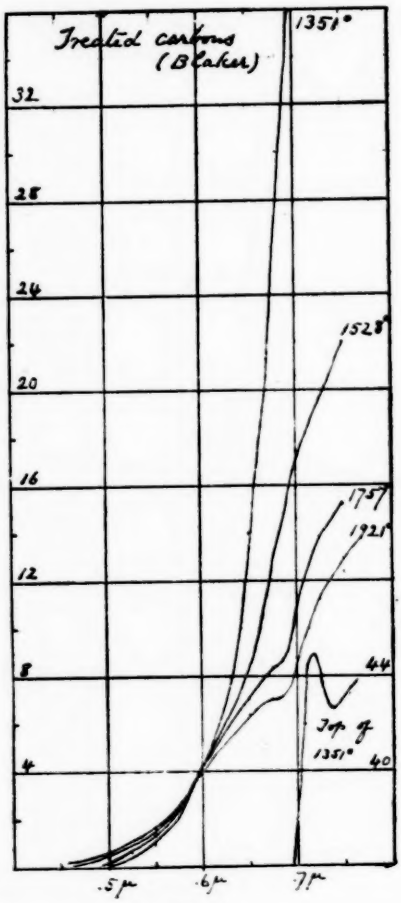

Fig. 4.

known silvery gray form of carbon characteristic of the treated filament of the incandescent lamp. Spectrophotometric measurements at temperatures from 1600° abs. upwards, showed the development of an interesting and unexpected deviation from the usual law

of radiation for carbon and this phenomenon was subsequently studied in much greater detail by Blaker.[1] As he likewise used the acetylene flame as a reference source in his measurements it is possible to reduce the spectrophotometric readings to absolute measure by means of the acetylene curve. The results, in form corresponding to that for untreated carbon in Fig. 3, are given graphically in Fig. 4. In these measurements, which were made upon the filament of an incandescent lamp, it was not possible to determine the temperatures directly by means of a thermo-junction as had been done in my investigation of untreated rods. The temperatures given are estimated by means of the relation between the resistance and temperature in such filaments as determined by Le Chatelier.[2] While it is not likely that the scale of temperatures in Blaker's work is directly comparable with those for the untreated

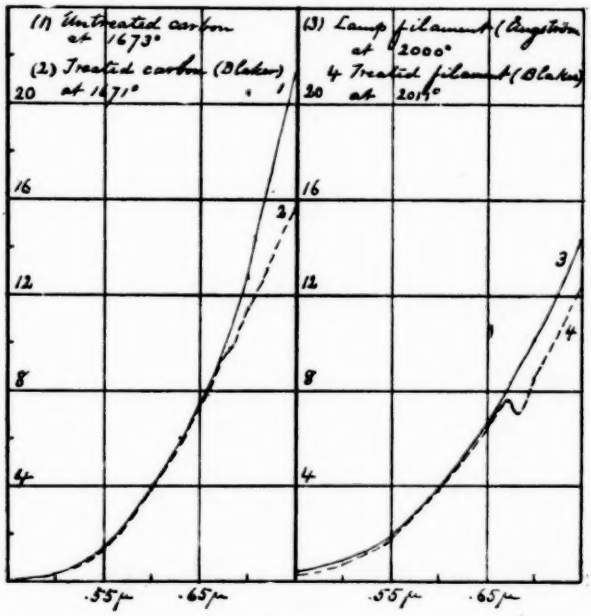


Fig. 5.

carbons, or with the temperature of the incandescent lamp measured by Ångström, it is at least instructive to compare the curves obtained. The curve for Blaker's lamp at 1671° abs. is accordingly plotted

[1] Blaker, *l. c.*

[2] Le Chatelier, Journal de Physique, (3), Vol. I., p. 203.

on the same scale as the curve for the untreated carbon rod at 1673° and the corresponding curve for Blaker's lamp at 2011° abs. with the incandescent lamp measured by Ångström (see Fig. 5). It will be seen that the curves are almost coincident as far as wave-length .65 $\mu$ beyond which the intensities for treated carbon fall off and the marked selective radiation of the latter begins to manifest itself.

## THE ELECTRIC ARC.

Although numerous spectrophotometric studies of the electric arc have been made, but few of these cover a sufficient range of wave-length to be available for the determination of the distribution of intensities throughout the visible spectrum. The three curves in Fig. 6 are from data (Table VI.) computed from measurements by Crova,[1] by W. S. Franklin and the present writer,[2] and from a comparison of the electric arc with the acetylene flame.[3]

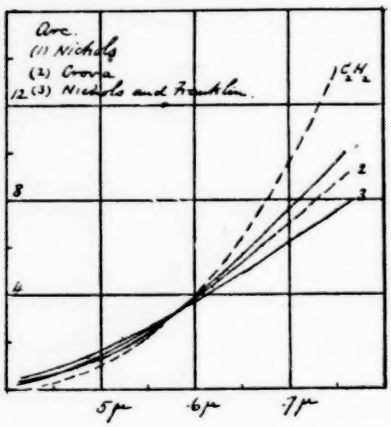


Fig. 6.

These curves show the type of radiation characteristic of incandescent carbon at very high temperatures, but the idiosyncracies

TABLE VI.

*Distribution of intensities in the spectrum of the arc light.*

| Wave-lengths. | Intensities from Comparisons by | | |
|---|---|---|---|
| | Crova. | N. & F. | N. |
| .45 | 0.90 | 0.67 | 0.65 |
| .50 | 1.35 | 1.47 | 1.67 |
| .55 | 2.38 | 2.55 | 2.59 |
| .60 | 3.96 | 3.86 | 3.73 |
| .65 | 5.66 | 5.30 | 4.87 |
| .70 | 7.65 | 7.03 | 6.28 |
| .75 | 9.60 | 8.68 | 7.55 |

[1] Crova, Comptes Rendus, 87, page 322.

[2] Nichols and Franklin, American Journal of Science, Vol. 38, p. 100.

[3] Nichols, Journal of Franklin Institute, Nov., 1900.

peculiar to treated carbon do not appear. The curve of distribution for the arc lamp will necessarily vary with the diameter of the carbons, the length of the arc, the current density and the angle which the line of sight makes with the axis of the lamp. The curves here presented refer to measurements taken under conditions such that light from all portions of the incandescent carbon was received upon the slit of the spectroscope. If the light from the crater alone were isolated, and its spectrum explored, a curve of much higher temperature would be obtained and we should expect to find the maximum of intensities lying within the visible spectrum. I am unfortunately not in possession of data for the computation of such a curve.

### Incandescent Oxides.

The sources of light of this class for which we have the necessary data, for the computation of the distribution of energy, are the

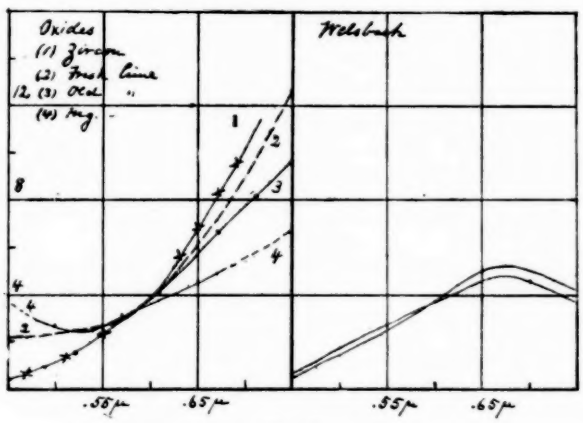


Fig. 7.

Welsbach mantel, the zircon light, the magnesium light and the lime light. The results are given in Table VII. and the corresponding curves in Fig. 7.

It was shown some years ago [1] that the light from the lime cylinder when first heated in the usual way by means of the oxyhydrogen flame differs greatly in character and intensity from that of the same cylinder after prolonged exposure to the action of the flame. These

[1] Nichols & Franklin, l. c.

TABLE VII.

*Distribution of Intensities in the Spectra of Incandescent Oxides.*

| From Comparison with the Hefner Flame (Koettgen's Data). | | | | From Measurements by Nichols and Franklin. | | | From Measurements by Rogers. | |
|---|---|---|---|---|---|---|---|---|
| Wave-Lengths. | Welsbach (I.). | Welsbach (II.). | Zircon. | Wave-lengths. | New Lime. | Old Lime. | Wave-Lengths. | Magnesium Flame. |
| .47 $\mu$ | 0.92 | 0.72 | 0.71 | .45 $\mu$ | 2.16 | 0.42 | .45 $\mu$ | — |
| .51 | 1.91 | 1.61 | 1.53 | .47 | 2.16 | 0.72 | .48 | 2.86 |
| .55 | 2.71 | 2.49 | 2.35 | .49 | 2.25 | 0.97 | .50 | 2.67 |
| .59 | 3.50 | 3.50 | 3.50 | .52 | 2.53 | 1.58 | .54 | 2.49 |
| .63 | 4.33 | 4.68 | 5.73 | .56 | 2.73 | 2.60 | .57 | 3.11 |
| .65 | — | — | 6.88 | .59 | 3.50 | 3.50 | .61 | 3.74 |
| .67 | 4.66 | 5.19 | 8.35 | .61 | 4.09 | 4.09 | .64 | 4.45 |
| .69 | 4.75 | 5.04 | 9.47 | .67 | 7.19 | 6.77 | .67 | 4.98 |
| .72 | 4.21 | 4.72 | — | .75 | '12.6 | 9.51 | | |

spectrophotometric measurements form the basis of curves 2 and 3 in Fig 7. Curve 2 represents the distribution of intensities of the freshly ignited lime. It differs from the various curves of incandescent carbon in the great excess of energy of shorter wave-lengths. The ordinate at wave-length .45 $\mu$ for example is about nine times as great as that of the Hefner flame and about four times as great as that of the arc in the same region. In the course of ten minutes after ignition the brightness of these portions of the spectrum suffers decadence, rapidly at first and then more and more gradually, and the distribution of energy in the spectrum goes over into the form indicated in curve 3. During this interval of time, however, what may be termed the permanent incandescence of the lime increases by the gradual heating up of the cylinder and the curve approaches nearly in form that of incandescent carbon; as may be seen by comparing curve 3 with the curves of the arc lamp. A detailed study of these changes has long since been described.[1] The curve of the Zircon light (1), Fig. 7; deduced from measurements by Koettgen, is identical with that for the old lime through the shorter wave-lengths of the spectrum but shows greater intensities in the red than either of the curves for the lime light.

The curves for the Welsbach or Auer mantels are from spectrophotometric studies made by Koettgen.[2] These mantels had been

[1] Nichols & Crehore, PHYSICAL REVIEW, Vol. II., p. 161.

[2] Koettgen, l. c.

in uninterrupted incandescence for twenty-four hours, after which time, according to observations of that investigator, they showed no further material change in spectral distribution. While these two mantels differed materially as to the quality of the light emitted, one being relatively stronger throughout the shorter wave-lengths and correspondingly the weaker in the red than the other, the type of the two curves is the same and they are altogether different from the other curves considered in this paper. The maximum intensity for the visible spectrum lies at wave-length .67$\mu$ but whether this is the maximum for the entire spectrum or a secondary maximum due to the selective radiation of the material can be determined only by the exploration of the infra-red.

The quantitative study of the spectrum of the magnesium light is difficult on account of the fluctuating character of the flame of magnesium even when burned in lamps with automatic feed. Spectrophotometric measurements of this spectrum have however been made by W. H. Pickering[1] and by F. J. Rogers.[1] From their results, which are in good agreement, curve 4 in Fig. 7 has been computed. Magnesium oxide is the only incandescent solid, for which we have any data, the energy in the spectrum of which is *greater in the violet than in the yellow and green.* It would appear from the form of the curve that there is a maximum in the ultra violet; a suspicion confirmed by the fact of the extraordinary actinic activity of this source of light. The type of the curve is similar to that for freshly ignited lime (curve 2), and it seems highly probable that if it were possible to make measurements upon lime at the instant of ignition, the curve would correspond still more closely to that of magnesia. It is possible to secure such measurements only in cases in which, as in the magnesium flame, the light is derived from the oxide at the instant of its formation by the combustion of the metal.

### Sunlight and Daylight.

Numerous spectrophotometric measurements of direct sunlight of the light reflected from the sky and in various conditions of the atmosphere have been attempted. Of these the measurements of

[1] Pickering, Am. Jour. of Science, 37, p. 100.
[2] Rogers, Am. Jour. of Science, Vol. 43, p. 301.

direct sunlight by H. C. Vogel,[1] W. H. Pickering,[2] W. S. Franklin and the present writer,[3] and by Koettgen [4] are in excellent agreement considering the varying atmospheric conditions. The determinations of Koettgen, who compared sunlight with the Hefner standard, have been adopted as the basis of computations for curve 2 in Fig. 8. His measurements extend through a greater range of wave-lengths and the comparisons are made with a source of light about which we have more definite information than is the case with the other available data. Measurements of daylight from cirrus clouds by the same writer have been selected for the same reason and the results of the computation are given in curve 3 of that figure. Curve 1 is from the direct spectrobolometric measurements of the sun's spectrum made by Langley.[5]

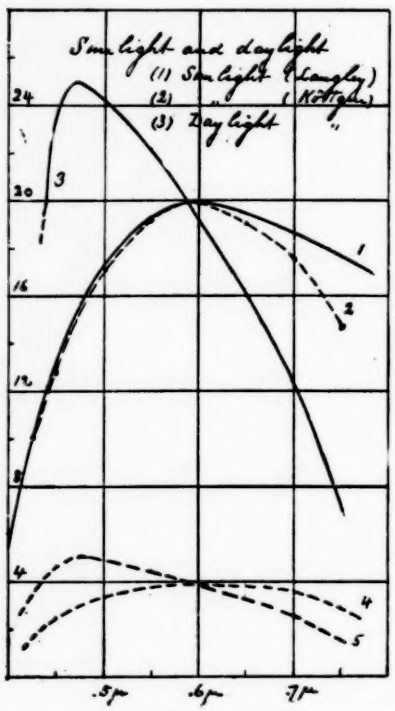

Fig. 8.

These curves are drawn with greatly increased ordinates. Plotted to the same scale as in previous figures curves 2 and 3 would appear as shown by the dotted lines 4 and 5.

It is noteworthy that curves 1 and 2 not only have the same maximum but are closely coincident excepting in the red. The divergence in that region is due to the selection of Langley's smoothed curve which was drawn tangent to the crests of the maxima in that region and so does not show the effect of atmospheric absorption.

[1] Vogel, Berliner Monatsberichte, 1880, p. 801.
[2] W. H. Pickering, Proc. Am. Acad. of Arts and Sicences, Vol. 15, 1880.
[3] Nichols and Franklin, American Journal of Science, Vol. 38, p. 100.
[4] Koettgen, l. c.
[5] Langley, Researches on Solar Heat, 1884, p. 139.

## A Comparison of the Energies of Visible Radiation.

The areas of the various curves of distribution of intensity, already described, taken between the red and violet limits of the spectrum, afford a measure of the total energy of luminous radiation from the sources of light to whose spectrum the curve applies. Ångström's value for the light energy of the Hefner standard flame is

$$20.6 \times 10^{-5} \frac{\text{grm. cal}}{\text{sec. cm.}^2};$$

the square centimeter of surface being situated at a distance of one meter from the flame in a horizontal direction. Reducing this numerical quantity to ergs, a more convenient unit for this purpose, we find that a square centimeter of surface at a distance of one meter from the Hefner flame receives *8.3 ergs per second* of light-giving energy. Assuming that the various curves in this paper

### Table VIII.

*Temperatures and ergs per lux-centimeter-second.*

| Source. | Ergs. | Temperature.[1] | | Source. | Ergs. | Temperature. | |
|---|---|---|---|---|---|---|---|
| Carbon rod (untreated). | 29.0 | 1273° abs. | *thj.* | Hefner flame. | 8.68 | 1934° abs. | P. |
| | 23.1 | 1373° " | | | | 1830° " | *A.* |
| | 17.8 | 1473° " | | Petroleum flat flame. | 8.69 | | |
| | 14.2 | 1573° " | | | | | |
| | 9.14 | 1673° " | | | | | |
| Lamp filament Ångström. | 7.26 | 2000° " | *A.* | Gas Triplex. | 9.13 | 1897° " | P. |
| | | | | Gas Batswing. | 8.40 | 2053° " | *thj.* |
| | | | | Gas Siemens. | 8.26 | | |
| | | | | Gas Sugg. | 7.70 | | |
| Lamp filament (treated). Blaker. | 18.5 | 1351° " | *Ch.* | Acetylene. | 7.12 | 2173° " | *thj.* |
| | 9.69 | 1528° " | | | | 2876° " | P. |
| | 7.38 | 1631° " | | Zicron. | 7.17 | | |
| | 7.34 | 1769° " | | Lime old. | 5.89 | | |
| | 6.35 | 1921° " | | Lime new. | 7.21 | | |
| | 6.42 | 2011° " | | | | | |
| Arc Nichols. | 5.92 | 4025° " | P. | Welsbach. (I.) | 4.39 | 2450° " | P. |
| Arc Crova. | 5.85 | | | Welsbach. (II.) | 4.50 | 2073° " | *thj.* |
| Arc N. & F. | 5.79 | 3690° " | W. & B.[2] | Magnesium flame. | 5.53 | 2258° " | *thj.* |
| | | | | Sunlight. | 4.85 | 5068° " | P. |
| | | | | Daylight. | 5.53 | | |

[1] Temperatures marked *thj.* have been determined by the thermojunction; *A.* by Ångström's method; *Ch.* by Le Chatelier's formula; P. by Paschen's equation.

[2] Waidner and Burgess, Physical Review, Vol. XIX., p. 241.

represent sources all of which are of equal photometric intensity (namely, one Hefner) so that in every case the illumination is one lux, the ergs per second received upon a square centimeter of surface at meters distance from each of the various sources of light in question will be given by multiplying the ratio of the area of the corresponding curves to the area of the curve for the Hefner flame, by 8.63. It has been assumed, as already stated, that curves plotted with equal ordinates for wave-length .59 $\mu$ correspond to equal photometric intensities of the sources. The areas of the curves thus plotted have been measured with the planimeter, and the results computed as just indicated are given in table VIII.

It will be seen from the table that the energy for unit illumination is by no means constant. In the case of sources of light whose radiation approximates to the law for a black body, that is to say for sources in which the incandescent substance is carbon, the energy per lux-centimeter diminishes with rising temperature; being 29 ergs per second for the carbon rod at 1273° abs., 7.12 ergs at the temperature of the acetylene flame, 5.92 to 5.79 ergs for the arc light and 4.85 ergs for sunlight.

Treated carbon, which has slightly selective radiation, shows decidedly smaller values than untreated carbon or than the carbon particles in flames. The metallic oxides, which are more strongly selective, furnish greater photometric intensity, per erg of luminous energy, than any of the sources in which carbon is the light-giving substance. Of these magnesium oxide, zirconium oxide and calcium oxide show very powerful selective radiation in the blue and violet, a region which is photometrically unimportant on account of the low luminosity of such waves. The selective radiation of the Welsbach mantel lies in a region near the maximum of luminosity and this source of light accordingly gives a larger photometric intensity per erg than any of the sources examined; namely, 4.39 ergs per lux-centimeter. The Welsbach mantel, however, owes its photometric superiority to a deficiency of red rays and to this deficiency the objectionable green color of this source of light is due.

It is noteworthy that of the incandescent bodies whose radiation approximates to the law for black bodies, the sun affords a maximum of photometric intensity per unit of luminous energy and that *the*

*maximum of the energy curve* of the sun's spectrum *coincides with the maximum of luminosity for the normal human eye.* Daylight

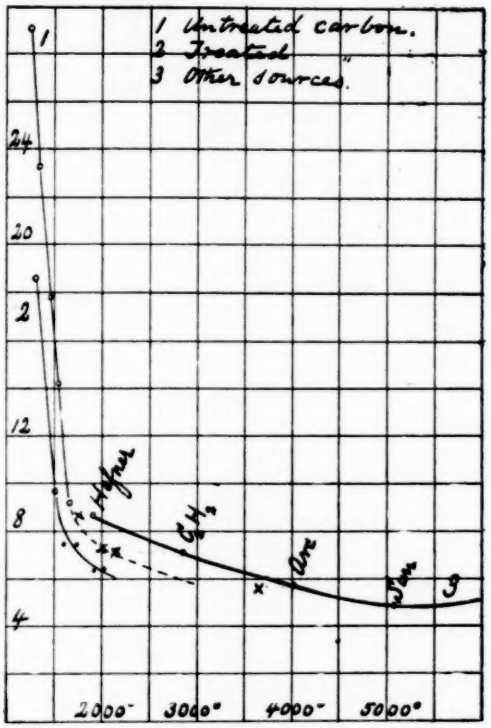


Fig. 9.

diffusely reflected from the sky, as in curve 3, Fig. 9, has a smaller photometric intensity per erg than direct sunlight.

## Relations between Temperature and Luminous Energy per Lux-centimeter.

It is obvious that there should exist, at least for sources having a common law of radiation, as in the case of carbon, a definite relation between the luminous energy per lux-centimeter and the temperature of the source of light. Estimates of the temperature of many of the sources already considered have been made by a variety of methods, but unfortunately the results are by no means consistent. If we take those sources for which the maximum of the energy curve has been determined and compute the absolute temperature from

Paschen's equation $\lambda_{max} T = 2{,}940$, we may plot a curve for which ordinates are ergs per lux-centimeter and abscissæ are temperatures (see curve 3, Fig. 9). Flame sources for which temperatures have been directly determined by means of the thermocouple or by Ångström's method will not fall upon this curve for the reason that absolute temperatures determined by means of Paschen's equation, using Lummer & Pringsheim's constant for a black body, are always much higher for such sources than those obtained by direct measure-

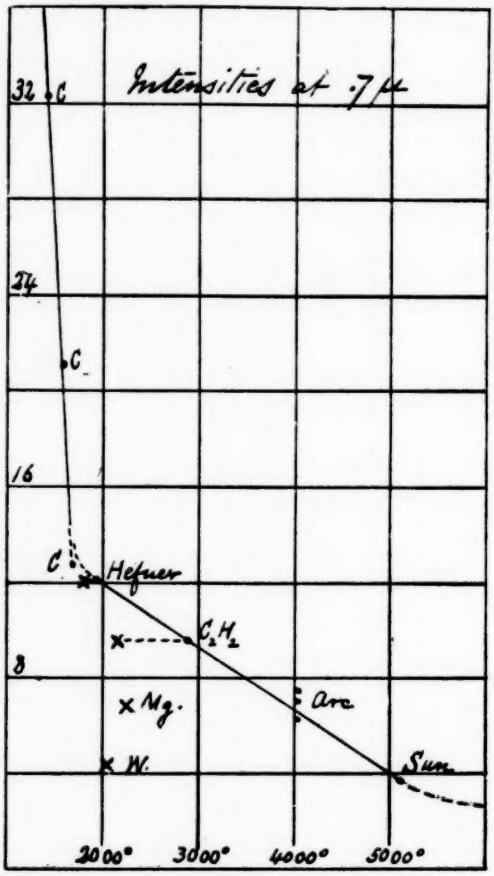


Fig. 10.

ment. The Welsbach mantel, on account of its peculiar selective radiation falls far below this curve, and the same is true of the flame of the magnesium ribbon as computed from the relative temperature found by Rogers.

In the case of the Hefner lamp, the acetylene flame and the arc, two positions are indicated upon the diagram. The round dots falling upon curve 3 are "$\lambda_{max}$" temperatures, the crosses connected with these by a dotted line are respectively the temperature of the Hefner flame as determined by Ångström, that of the acetylene flame from measurements with the thermojunction and the temperature of the arc according to Waidner and Burgess. It seems certain from this figure that if we had consistent measurements of temperature for a body such as carbon between 1200° abs. and the temperature of the arc, the curve would show a sharp inflection at about 1700°. There are definite indications of such a trend in curve 2 for treated carbons and although the measurements with the thermojunction for untreated carbon do not carry us past the point of inflection, the lamp filament measured by Ångström at 2000° abs. lies nearly upon a continuation of curve 1.

If instead of taking the ergs per lux-centimeter we plot the intensity of the spectrum of these sources of light at wave-length .7 $\mu$ as a function of the temperature, the ordinates being in each case those which correspond to an illumination of one lux at meters distance, we get the curve shown in Fig. 10, which has an inflection point at the same temperature. Magnesium oxide and the Welsbach mantel, indicated respectively by the crosses "Mg" and "W," lie far below the curve for the carbon sources and it is evident that in optical pyrometry, where the variation of intensity of red light is used in the determination of the temperature of such a source, the "black temperature" will be very much higher than the actual temperature of the glowing body.

PHYSICAL LABORATORY OF CORNELL UNIVERSITY,
December, 1904.

# THE RANGE OF ADJUSTMENT FOR THE CONICAL PENDULUM.

BY FREDERICK SLATE.

WITH the usual arrangement of a conical pendulum, the equation of adjustment for steady motion can be put into the form,

$$\omega^2 \sin\gamma \cos\gamma \,(I_A - A_B) = -mgy. \qquad (1)$$

Here $\gamma$ is the semi-angle of the cone described by the line joining the hinge $(H)$ and the center of mass $(C)$; $\omega$ is the constant angular speed about the vertical axis of rotation $(HX)$; $I_A$ and $I_B$ are moments of inertia for the principal axes in the plane of the figure at the point $H$, $HA$ being often in practice an axis of symmetry. The length $HC$ is $r$, such that $r^2 = x^2 + y^2$. When adjustment exists, weight and the force distributed from the hinge have for their resultant the system of normal forces, of the type $dN = -dm\rho\omega^2$. And equation (1) expresses directly, for the hinge-axis, the necessary equality of moments between resultant and components, since one component, in this case, can contribute nothing to the moment.

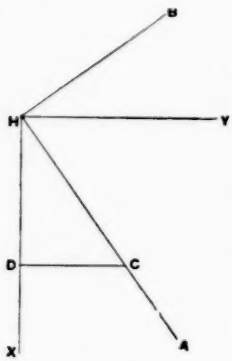

Fig. 1.

Evidently $\sin\gamma = 0$ satisfies the equation for all possible values of $\omega$. Rejecting the factor corresponding to this solution, there remains in general a second solution, given by

$$\cos\gamma = -\frac{mgr}{\omega^2(I_A - I_B)}. \qquad (2)$$

If the ratio in the second member equals unity, the two solutions agree. But so long as $\omega^2(I_A - I_B)$ is numerically greater than $mgr$ there is a second real value of $\gamma$. This value is $\pi/2$, if $r$ is zero; otherwise, $HC$ lies above or below $HY$, according to the relative

magnitudes of $I_A$ and $I_B$. When $r$ is not zero, and $I_A = I_B$, $\gamma$ becomes imaginary, as an expression of the fact that every line through $H$ in the plane $XY$ is then a principal axis, and all constraining moment is then superfluous at any angle $\gamma$. But there is a general failure to recognize and interpret the remaining imaginary values of $\gamma$, which present themselves when $\omega^2(I_A - I_B)$ is finite, and numerically less than $mgr$. There may be an instinctive assumption that $\gamma$ and $\omega$ are in continuous real relation, because $\gamma = 0$, $\omega = 0$ are corresponding values, while other real pairs are observable at finite angular speeds. But this instinct overlooks the truth that $\gamma = 0$, $\omega = 0$ is a pair belonging to the solution $\sin \gamma = 0$. What may interest us, therefore, is to examine *the gap between the solutions*, supposing the inertia constants of the body and the length $HC$ given, the latter different from zero, and $\omega$ increasing continuously from zero.

The physical conditions are easily connected with the rectangle $(xy)$, which may be taken, as shown below, to represent, at any position, either the weight moment, or the aggregate moment of the distributed normal forces. In general, of course, the proportional factors for the two force moments thus represented by the same area will be differerent. Adjustment to steady motion, then, corresponds to equality of the proportional factors; and the imaginary values of $\gamma$ that are here in question will fall within the range where this equality becomes impossible. Let us proceed to determine those factors. For weight moment in any position, the factor $(a)$ is given by the relation

$$axy = -mgy; \quad a = -\frac{mg}{x}. \tag{3}$$

For the normal forces, with the factor $(b)$, the necessary relation is

$$bxy = -my\omega^2 \cdot x_1; \; b = -m\omega^2 \frac{x_1}{x}; \tag{4}$$

since, for the assumed symmetry, the resultant of the normal forces must be a force $my\omega^2$, inward (*i. e.*, parallel to $YH$), at a distance from $H$ here denoted by $x_1$. Now, from

$$-my\omega^2 \cdot x_1 = \omega^2 \sin \gamma \cos \gamma \, (I_A - I_B),$$

we obtain, by simple reduction,

$$-\frac{x_1}{x} = \frac{I_A - I_B}{mr^2}; \quad b = \frac{\omega^2}{r^2}(I_A - I_B). \tag{5}$$

Therefore, while the one factor ($a$) begins at the value $mg/r$ (for $\gamma = 0$), and increases toward infinity as $x$ decreases from $r$ toward zero, the other factor ($b$) begins at zero ($\omega = 0$), and increases toward infinity with increasing angular speed. No adjustment is possible until the numerical value of the second factor has *overtaken* that of the first. Corresponding to the condition $a = b$, we find

$$\frac{mg}{x} = \frac{\omega^2}{r^2}(I_B - I_A),$$

whence

$$\omega^2 = \frac{mgr}{\cos\gamma\,(I_B - I_A)}. \tag{6}$$

And, for the critical minimum value of the angular speed,

$$\omega\,(\text{min.}) = \pm\sqrt{\frac{mgr}{I_B - I_A}}. \tag{7}$$

For values of $\omega$ less than this critical value, we have $b < a$, at the smallest value of $a$, and the weight moment is in excess of the requisite constraint; $HC$ drops back to $HX$ from any angle of divergence, however small.

When the rotating body has equal moments of inertia for $CA$ and for a parallel to $HB$ at $C$, equation (6) assumes the simplified form,

$$\omega^2 = \frac{g}{r\cos\gamma}. \tag{8}$$

In connection with this, it is furthermore easily seen that the impossible values here discussed would necessitate a vertical component of the hinge-force less in magnitude than the weight to be supported; or, otherwise expressed, a perpendicular ($HD$) in the force-triangle ($HDC$), longer than the hypotenuse ($HC$).

UNIVERSITY OF CALIFORNIA.

# THE EVOLUTION OF NITROGEN FROM THE CATHODE AND ITS ABSORPTION BY THE ANODE IN GASES.

By Clarence A. Skinner.

RESULTS of experiments have been published recently in the Physical Review,[1] showing the rate of evolution of hydrogen from the various metals when used as cathodes in helium, and also its rate of absorption by the anode when the gas filling is hydrogen. It was found that a fresh cathode gives off hydrogen at the same rate as a water voltameter conceived to be placed in series with the discharge tube, that is the rate of evolution follows Faraday's law for electrolytes. This held with pressures of helium varying from 1 to 3 mm.; with currents varying from 1 to 3 milliampères; and finally with current densities varied from one to six times the *normal* value for the cathode, and with which also was associated a change in cathode fall of about one hundred volts. Then assuming that the evolution in hydrogen was the same as in helium results were given showing that with the hydrogen filling the anode absorbs gas also at a rate following Faraday's law. After the current has passed for a time the rate at both cathode and anode falls below Faraday's law. This is to be expected.

It appeared remarkable that the gas given off by the various cathodes was in all cases hydrogen. Only occasionally was the presence of nitrogen also noted. It is important to know, however, if other gases possess in this respect the same properties as hydrogen. The present paper is a report of the experiments showing that nitrogen plays the same part in carbon electrodes that hydrogen plays in the metals. In addition, observations are given showing that a metal as anode also takes up nitrogen.

First will be given a description of some experiments which led up to the investigation of nitrogen, as the results are of importance in that they reveal the source from which the metals obtain their

[1] Clarence A. Skinner, July, 1905.

supply of gas, and further that a metal cannot be freed entirely of absorbed gas by use as cathode.

The object of these experiments was to obtain a metal free of absorbed gas. Zinc, which has rather a low boiling point, was distilled in glass combustion tubing in an atmosphere maintained by continuous pumping at about .2 mm. pressure. After distillation it was removed, worked into the required form by a clean cutting-tool, then mounted with a similar electrode of ordinary zinc in the electrode tube. This tube was thereupon evacuated and allowed to stand in connection with a drying chamber over night. Tested as cathode the next day in helium the distilled zinc was found to give off hydrogen at the same rate as the one that had not been distilled. It had evidently gained a supply from the necessary exposure to the atmosphere, as it would hardly be expected to hold hydrogen at the temperature and gas pressure at which it had been distilled. Thinking therefore that it must be largely a surface occlusion the electric current was maintained from it as cathode with the hope that soon all gas might be driven off. An interrupted run extending over ten days proved this to be a fruitless undertaking. The evolution of gas decreased to an almost inappreciable quantity, but a spectroscopic observation of the cathode revealed, to the last, hydrogen and nitrogen lines which were clearly marked though less brilliant than those of the helium. The nitrogen radiation was almost wholly absent during the first run of about an hour, but with successive tests gradually grew brighter, remaining finally but little changed in intensity after the hydrogen radiation had diminished perceptibly. The gas filling during these runs was repeatedly purified by a Na,K cathode discharge. This proved after a time ineffective, so the old Na,K discharge tube was replaced by a fresh one. This change necessitated the admission of air for a short time to the electrode tube. Then having been left evacuated over night a test the next day showed that the zinc had regained a new supply of gas which differed in no perceptible way from the first. These experiments prove therefore that a discharge from the metal as cathode will not wholly free it of absorbed gases, and that the metal obtains a supply by exposure to the atmosphere, of which it is very likely that moisture is a necessary part

The persistent presence of nitrogen in the distilled zinc, though the quantity given off was small, suggested the possibility of obtaining quantitative results with this gas if carbon, which absorbs it in large quantities, be used as cathode.

### Experiments with Carbon Cathodes in Helium.

A detailed description of the apparatus used is given in the paper to which reference has already been made. Briefly, it consists of an electrode tube in which can be mounted several electrodes in form of circular disks inlaid in glass. These may be used one after the other without opening to the atmosphere. The gas used as filling is admitted through a stop cock and its pressure measured by a MacLeod gauge.

Three carbon disks (15 mm. in diam.) cut from hard arc-carbon were mounted in the electrode tube and this was evacuated and left over night connected with a drying chamber. The next day the slight amount of gas which had been given off was pumped out and helium admitted to a pressure of about three and a half millimeters. With an aluminium disk serving as anode and one of the carbon disks as cathode, a current of 2 ma. was passed through the helium. A spectroscopic observation of the cathode revealed a gradually brightening nitrogen radiation in addition to that of helium. A trace of hydrogen was also observed. The increase in gas pressure with the time the current had been flowing was noted. The results are represented by curve 1 in Fig. 1. If with a helium filling there is no absorption by the anode the quantity of nitrogen given off under the discharge may be calculated from the pressure increase and the volume occupied by the gas, 465 c.c. For making a comparison the direction of the line $F$ represents in the figure the rate of increase in pressure required by Faraday's law.

After the above observations, extending over fifteen minutes, were made, the electrode tube was evacuated and fresh helium admitted. A similar test of the second carbon disk, in helium at 3.1 mm. pressure, gave the results represented by curve 2; while from the third disk (gas pressure 3.2 mm.) curve 3 was obtained.

During the first three minutes these different curves diverge widely but over the rest of their extent all three are very nearly parallel

to each other, and also, between three and five minutes, they approach closely to the direction of *F*. Beyond the five-minute point their inclination gradually drops below that of *F*. It is probable that during the first three minutes, owing to the increase in temperature of the cathode surface, uncharged gas is also freed from the cathode, the quantity depending on its concentration in the carbon. The fact that all three curves run parallel to each other beyond this point, and at this point are also parallel to *F*, indicates that the liberated gas carries as negatively charged atoms all of the current between cathode and helium for the first five minutes of discharge.

As observed with metals, carbon also recovers a supply of gas by diffusion from within. Immediately following the series of observations just described the electrode tube was evacuated, then after a six hour's rest, the first carbon tested again. The results were identical with those obtained in the first series from the second carbon. They are represented by crosses on curve 2.

### EXPERIMENTS WITH CARBON ELECTRODES IN NITROGEN.

Experiments with metals having shown that in a hydrogen-filling the metal as anode absorbs hydrogen according to Faraday's law, similar experiments with carbon in a nitrogen-filling were performed.

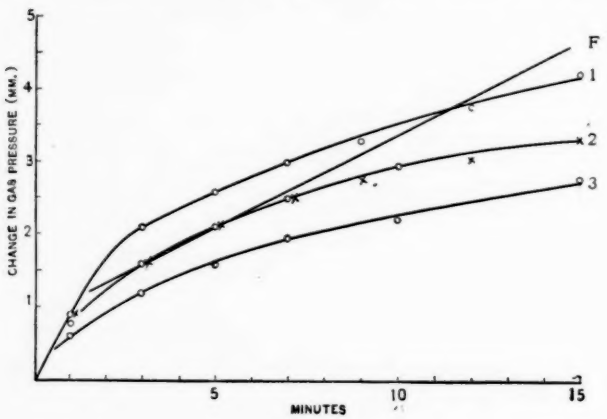


Fig. 1.

Two carbon disks of equal discharge area were used as electrodes and a current of 2 ma. was passed through nitrogen (1.8 mm.).

The change in gas pressure with time of flow for two separate experiments is represented by curves 1 and 2 in Fig. 2. No trace of hydrogen could be detected in either case. The gas pressure rose for a time differently in the two experiments, but reached a maxi-

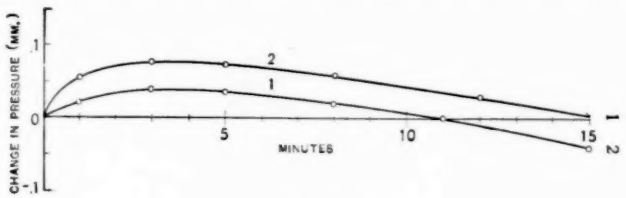


Fig. 2.

mum value for both at the same time (three minutes). It then decreased at the same rate in both up to the end of the fifteen-minute run. These results appear nearly related to those obtained in helium.

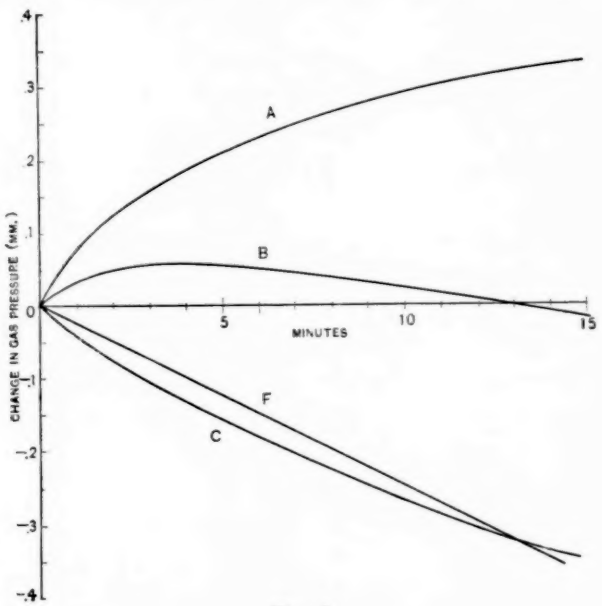


Fig. 3.

Separate experiments give here as there divergent results for the first three minutes but after that time they agree closely.

If now a carbon anode does not absorb helium, and a carbon cathode gives off gas at the same rate in nitrogen as in helium, the

effect of the carbon anode in nitrogen is what causes the difference in form between the curves of Fig. 1 and those of Fig. 2. In Fig. 3 curve $A$ is the mean of those in Fig. 1, and curve $B$ the mean of those in Fig. 2. $B$ therefore represents the combined effect of carbon electrodes in nitrogen, while $A$ is assumed to represent that of the cathode alone. Now if $A$ be subtracted from $B$ the resultant curve $C$ shows the absorption of gas by the anode. This curve lies unexpectedly close to the direction of the Faraday law line $F$ over the whole range. Its absolute value however is too great owing to the wide divergence in results from the separate experiments for the first three minutes of current. The close agreement exhibited by these after that time makes the results however reliable. For seven minutes at least we conclude that the carbon anode takes up all nitrogen atoms discharging to it. The concentration then reaches such a magnitude that uncharged gas is given off by it at a gradually increasing rate.

### EXPERIMENT WITH A CARBON CATHODE AND AN ALUMINIUM ANODE IN NITROGEN.

Since nitrogen is contained to only a very slight extent in metals it is of interest to know if they take it up when used as anode in it. An experiment was performed with two points in view. The first was to decrease if possible anode absorption in nitrogen in order to prove that a carbon cathode evolves gas at the same rate

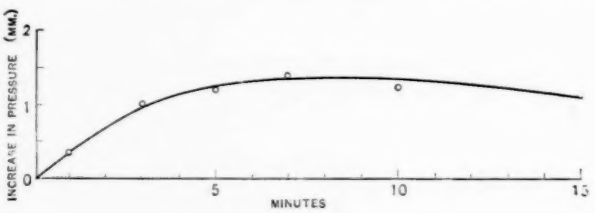


Fig. 4.

in nitrogen as in helium. The second was to test if the metal as anode does take up nitrogen.

With a carbon disk as cathode and an aluminium anode of less than one twentieth its area a current of 2 ma. was passed through nitrogen (1.9 mm.) and pressure measurements made as before.

The results are represented by the curve in Fig. 4. The aluminium surface during this run turned to a dusty brown color as if there were chemical union taking place between metal and gas instead of a physical absorption. The gas pressure increased more rapidly than when either of the carbon anodes were used. A maximum value was reached at seven minutes after starting, instead of three; then a slight decrease in pressure, less rapid than with carbon took place. A comparison of this curve with those of Figs. 1 and 2 indicates that as anode absorption in nitrogen decreases, the pressure curve in nitrogen approaches toward that obtained in helium — this supporting the assumption already made that the amount of gas given off by the cathode is the same in nitrogen as in helium.

## General Discussion.

*Present Experiments.*— The results of these experiments with carbon electrodes in helium and nitrogen support in a very satisfactory manner the conclusions suggested by the experiments with metal electrodes in helium and hydrogen, so more general conclusions may in turn be suggested.

With a gas-filling which is chemically neutral and is not absorbed by the substance composing the electrodes, the electric current between cathode and gas-filling is carried by negatively charged atoms of gas which are already to be found in solution in the cathode. These negative atoms give up their charge to the gas-filling by neutralizing positive ions of the gas-filling. If the cathode possesses a sufficient supply of absorbed gas this neutralization takes place outside the cathode indicated by the fact that the gas pressure increases at a rate demanded by Faraday's law. If, however, the absorbed gas falls below a definite concentration it does not go out of the cathode at a rate sufficient to carry the whole current, but this is probably made up by the positive ions of the gas-filling penetrating the cathode and discharging to the absorbed gas inside, just as in the other case, they discharge to it outside the cathode. If these penetrating ions be chemically and physically neutral they will diffuse back uncharged into the gas-filling. This view explains the fact that evolution of gas from the cathode falls after a time below Faraday's law. If the gas-filling be one which remains in absorption

in the cathode the penetrating positive ions may, after discharging to the absorbed gas, play in their turn the part of the absorbed gas in transmitting the current, and results, so far as pressure change is concerned, become more complicated.

At the anode absorbed gases are conceived to play a minor part. Just as it appears impossible for a positively charged gas ion to discharge directly to the cathode, so it is considered impossible for absorbed gas atoms in the anode to carry off from it positive electricity. This could only take place by atoms (or particles) of the anode itself, or at least by some absorbed substance, which in electrical union with the substance composing the anode, is positively charged, while the metal atoms are negatively charged. We conceive therefore that, in the main, the current between anode and gas is carried by negative ions of the gas-filling discharging directly to the anode. If these be atoms of a neutral gas (*e. g.*, helium) they diffuse back without charge into the gas-filling. If they are atoms which form a physical or chemical union with the anode substance they will stick to the anode until such a concentration is reached that they are given off again uncharged. This explains the fact that the anode does not affect the gas pressure when helium is used as a filling, but in hydrogen and nitrogen absorption takes place there at a rate determined by Faraday's law.

The basic principles on which these explanations rest may be summed up as follows:

(*a*) With the existence of chemical affinity or the tendency to form a physical solution, the charging and discharging of a gas atom takes place with one kind of electricity but not with the other (*e. g.*, hydrogen and nitrogen will receive from a metal and give up to it a negative charge, but neither receive nor give to it directly a positive charge).

(*b*) With the absence of both chemical affinity and a tendency to form a physical solution negatively charged gas atoms readily discharge to a metal but those positively charged do not.

(*c*) Without the existence of chemical affinity gas atoms carrying charges of opposite sign transmit a current by mutual discharge, separating thereafter uncharged.

If, therefore, a gas be found which, when absorbed by a conductor,

becomes positively charged, the conductor negative, we should expect to find cathode and anode phenomena (including electrode fall) interchanged.

*Electrode Fall.*— An explanation of the great difference in the fall of potential at cathode and anode may be suggested here. The negative gas ion simply discharges to the anode, either being absorbed by it or falling away uncharged. At the cathode either the negatively charged gas must be driven out of it or the positive ions driven into it (to meet the absorbed negative atoms) at a rate sufficient to carry the current. In addition, therefore, to the energy-change by simple absorption or combination at the anode there is at the cathode that absorbed in forcing the charged gas atoms to diffuse through the metal. This appears to be caused by the positive gas ions, under the electric forces bombarding the cathode surface and thereby maintaining a molecular agitation equivalent to that produced by heat. The cathode fall should therefore increase: (*a*) with the resistance to diffusion through the cathode; (*b*) with depletion of absorbed gas in the cathode; (*c*) with the energy required to maintain the dissociation of the gas-filling so that bombarding atoms be furnished. (This latter would therefore increase with the rate of recombination of the dissociated gas.) The energy of absorption of gas by the cathode would also play a part so long as its concentration in the cathode is changing.

The anode fall in nitrogen has been found to increase with use. Copper is a marked example.[1] This probably arises from the increase in concentration of absorbed gas, for use as cathode has been observed to cause the anode fall to return to its original value. Further, Warburg[2] found that if a steel cathode possesses an oxidized surface the cathode fall is thereby greatly reduced so long as the oxide remains. In such a case the current is probably carried by negatively charged oxygen emanating from the surface instead of by gas atoms diffusing out of (or into) the body of the metal. The resistance to diffusion would thereby be greatly decreased. If however the heat of combination of oxygen with steel be greater than that of absorption of hydrogen this latter would tend to neutra-

[1] C. A. Skinner, Wied. Ann., 68, p. 752.
[2] E. Warburg, Wied. Ann., 31, p. 545.

lize the effect of decreased resistance to diffusion. It is likely, from comparison with the anode fall, that resistance to diffusion in the metal plays generally a much greater part in determining the cathode fall than does energy of absorption (or combination).

This view of the cause of the electrode fall requires that the cathode fall should disappear when the cathode is raised to a temperature that will drive the absorbed gas out of the cathode at a rate sufficient to carry the current. Cunningham has shown that the cathode fall of carbon in rarefied gases decreases as its temperature rises.[1] Wilson[2] has found that hot platinum fails to give of negative electricity when freed of absorbed hydrogen. It is probable therefore that the negative leak from incandescent carbon would disappear if the carbon were completely freed from absorbed gases. Conduction in flames is also greatly facilitated by heating the cathode. Stark and Cassuto have shown that in order to maintain an electric arc the cathode must be at a high temperature while the temperature of the anode is of no effect.[3] It is also known that in the ordinary arc the cathode fall is very small while the anode fall is of the same magnitude as with the glow discharge through rarefied gases. While however the principles enunciated above will apply to the electric arc it is probable that much of the current between the electrodes is carried by the substance composing them. Stark concludes from experiments on the mercury arc that the mercury vapor emanating from both electrodes carries the current — that from the anode carrying positive, that from the cathode negative electricity.

*Photoelectric Currents.* — The same reasoning followed above in regard to the effect of cathode temperature applies to the effects of light and other radiations on conduction through gases when these radiations fall on the electrodes. The absorbed gas may be freed from both electrodes but only that leaving the cathode can act as carrier of the current. The gas absorbed in the anode cannot receive from it a positive charge therefore must leave either charged negatively or uncharged, but since the anode is positively charged the negative ions of the gas would be held by it and hence only

[1] J. A. Cunningham, Phil. Mag., February, 1905.
[2] H. A. Wilson, Phil. Trans., 202, p. 243, 1903.
[3] N. Cimento, June, 1904.

uncharged atoms escape. On the other hand at the cathode the negative ions after being freed would be driven forth by the electric forces. We have thus the radiation affecting conduction when it falls upon the cathode but not upon the anode.

*Conduction of Gases in Vicinity of Metals*— It is possible that this may arise at least in part from absorbed gas atoms emanating from the metal. It is known that a sodium-potassium alloy discharges conductors placed in its neighborhood. Now the writer has observed that even after distillation in vacuo pure hydrogen is continuously given off by this alloy. A series of observations extending over more than ten days, with two different samples of it, showed that from about seven square centimeters of surface .1 to .2 c.c. of hydrogen (at atmospheric pressure) is liberated per day when the gas pressure is kept very low. There seemed to be no reduction in quantity liberated as time passed but a variation in daily temperature appeared to cause a change in the quantity given off. Neither sample had a clean metallic surface; both had become tarnished by oxygen and nitrogen.

*Contact Potential.* — The writer has recently published[1] experimental results showing that a close relationship exists between the series of metals arranged according to the magnitude of their electrode fall in gases and the contact potential series. This is especially marked in case of the cathode fall in hydrogen. The two series are practically identical. It is therefore probable that an explanation of the one will also furnish the principles upon which the other is explicable.

We have concluded that in gases positively charged ions will not discharge directly to a conductor while the negative ions give up their charge readily and with it are generally absorbed. If therefore two metals be placed in an ionized gas together, the positive ions will remain in the gas while the negative are absorbed at a certain rate by the metals. The metal which absorbs these most rapidly becomes negatively charged with respect to the other. This difference in charge increases until the difference of potential between them produces a sufficient electromotive force to cause absorption in both to take place at the same rate. After that there

[1] Phil. Mag., September, 1904.

is no further change in potential difference of the two metals. For example, aluminium which becomes, in contact with platinum, negatively charged, is supposed to absorb the negative ions in the gas-filling more rapidly than platinum. This agrees with the results in rarefied gases; for, tested as cathode in gases aluminium is found to give up hydrogen more freely than platinum does and also as a consequence of this possesses a lower cathode fall.

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# THE RESIDUAL ELECTROMOTIVE FORCE OF THE CARBON ARC.[1]

By G. G. Becknell.

IN the course of some recent experiments on unipolar conductivity between metallic plates, it was suggested to me by Professor Crew that I examine the somewhat similar case afforded by the intensely heated region between the electrodes of a carbon arc *immediately after its interruption.*

The circuit was so arranged that the dynamo and galvanometer could, by means of a double-pole double-throw switch, be alternately joined in series with the arc-gap. (See Fig. 1.)

It was found at once that a current, which we may call the *residual current*, could be observed for more than ten seconds after the interruption of the arc; and it was seen, upon replacing the galvanometer by a Weston voltmeter, that the residual electromotive force was counter to that of the dynamo, and reached a maximum value of more than half a volt.

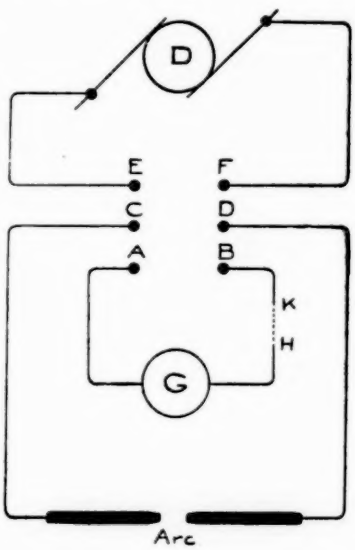

Fig. 1.

In order to show something of the qualitative nature of the phenomenon, the following simple experiments were tried:

1. A plate of either copper or mica, *i. e.*, a plate of material either conducting or non-conducting, when interposed between the electrodes without touching either of them, was sufficient to arrest the residual current entirely; but upon the removal of the plate the current was immediately reëstablished.

[1] A paper read before the American Physical Society, April 21, 1905.

This experiment with the copper plate shows that the residual effect can hardly be due to thermo-electric contact (whatever that may mean) between the heated carbon tips and the heated gases of the arc, for in such a case the interposition of a copper plate across the arc-gap would tend to increase the current through the galvanometer, and certainly not to destroy it.

2. A short copper wire joining the positive and negative electrode was sufficient to stop entirely the residual current *through the galvanometer*, showing that the effect cannot be traced to a thermo-electric source existing *outside* the arc, for in this event the current would have been much increased by thus cutting out the resistance of the arc-gap. We may fairly conclude then, perhaps, that the residual current is due neither to a thermoelectric effect in the arc nor to one external to it.

3. As a further test a gentle air-blast was applied to the region between the carbons at the instant when the galvanometer was thrown into the circuit. This again had the effect of removing nearly all traces of the residual current as long as the air current was continued, unless the poles were placed as nearly together as one millimeter, and even then the effect was reduced to one tenth. The failure at this point to completely destroy the effect was probably due to the partial inaccessibility of this small region to the current of air. It was found also that when the air-blast was discontinued the residual current was set up again, provided the blast had not been applied for a time longer than four or five seconds.

4. It was observed also that if the galvanometer was thrown off and the dynamo thrown on to the arc-gap for a few seconds, thus producing an electric field, *but no arc*, between the electrodes, a smaller residual current was reëstablished in the same direction as before, that is, counter to that of the dynamo. This effect could be detected if tried within a minute or two after the interruption of the arc.

It would seem from these experiments—the interposition of the mica sheet, and of the readily conducting copper, as well as the effects of the air-blast, and the renewal of the electric field, that we have here not a case of ordinary electric *conduction*, but probably

one of electric *convection*. This view is strengthened by the fact that the *alternating* arc gives a very small residual effect.

In attributing this current to convection it is not meant to imply that this is an explanation of the phenomenon. On the contrary the ionic explanation of it, which I shall offer at the close of this article is not entirely satisfactory, or at least is not complete.

Now passing to the quantitative side of this phenomenon, I proceeded as follows to measure the residual electromotive force and current as functions of the time.

A rotating switch of special design was employed to automatically break the dynamo circuit at any desired instant, then after a definite and measurable interval which might be varied at will, to throw the galvanometer into circuit with the cooling arc-gap for a definite fixed period which also might be varied if desired.

This rotating switch consists essentially of two similar vulcanite discs fitting face to face, each graduated in degrees, and capable of being set in any desired phase with relation to one another. Both are clamped to a shaft by means of a lock-nut, and the device is kept in uniform rotation with a period of ten seconds by means of a constant-speed motor. On the outer face of each of the disks is inlaid a silver strip of particular design, each strip passing under its own metallic brush.

One of these strips, coming into contact with its corresponding brush closes the circuit of an electro-magnet which acts upon a wooden rocker-arm, and thus through mercury cups connects the arc with the dynamo for a definite interval.

As soon as the first silver strip passes off its brush the circuit of the electro-magnet is broken, the rocker-arm is released and drawn away by a spring cutting out the dynamo circuit at $EC$ and $FD$, in Fig. 1, and closing the mercury cups $AC$ and $BD$; so that as soon as the second strip passes under its corresponding brush, the galvanometer circuit is closed at $GK$ at the proper time and during the proper interval.

At the very outset it was observed that the length of time the arc is allowed to burn before measuring the residual electromotive force is a very important factor. A steady state seemed to be reached in about one minute, and all my observations have been made after waiting this length of time.

The arc was used in the vertical position, in which it was found to behave in a much more uniform manner than in the horizontal position.

It was found, furthermore, that the magnitude of the residual current is somewhat dependent upon the quality of carbons used. For example, graphite terminals were observed to produce a very small residual effect; however this may have been due to the unsteadiness of the arc.

If results are to be uniform, and the effect to be as great as possible, it is absolutely necessary that the arc be centered, and that it should not be running about the electrodes.

Filing the carbons to a definite shape adds further to the constancy of results, for in this case the arc potential difference, arc current, and pole distance can all be held constant throughout the experiment.

In order to determine the residual electromotive force and current as functions of the time, null methods were employed. The measurement of the electromotive force was effected by means of a Wolff potentiometer, thus balancing the average value of the varying electromotive force during one tenth of a second, against another constant and known electromotive force applied for the same length of time.

In a similar way the varying current was balanced against a known constant current, by the use of a differential galvanometer.

The curves shown in Figs. 2 and 3 were thus determined, cored carbons having a diameter of 1.6 cm. being employed. These carbons were purchased from the Western Electric Co. of Chicago. The impressed electromotive force was 110 volts, the potential difference of the arc 35 volts, the arc current 16 amperes, and the pole distance 4 mm. Both curves rise rapidly within the first quarter of a second, the electromotive force reaching a value of nearly 0.65 volt, and the current a value of 0.55 mil-ampère through a circuit containing 1,000 ohms in addition to the arc resistance. The descent of the current is much more precipitate than that of the electromotive force, showing that the resistance of the arc increases very rapidly.

A very interesting thing is noticed in the behavior of the differ-

ential galvanometer when a point upon the rising portion of the curve is being studied. In this case the instrument first gives a twitch in favor of the battery, then immediately after one in the direction due to the arc, thus indicating a rapid rise at the point under consideration. On the falling side of the curve the deflections occur in the reverse order.

The interesting study of the counter electromotive force of the arc which has already been presented to the American Physical Society by Mr. Hotchkiss,[1] as well as that of Blondel,[2] is confined

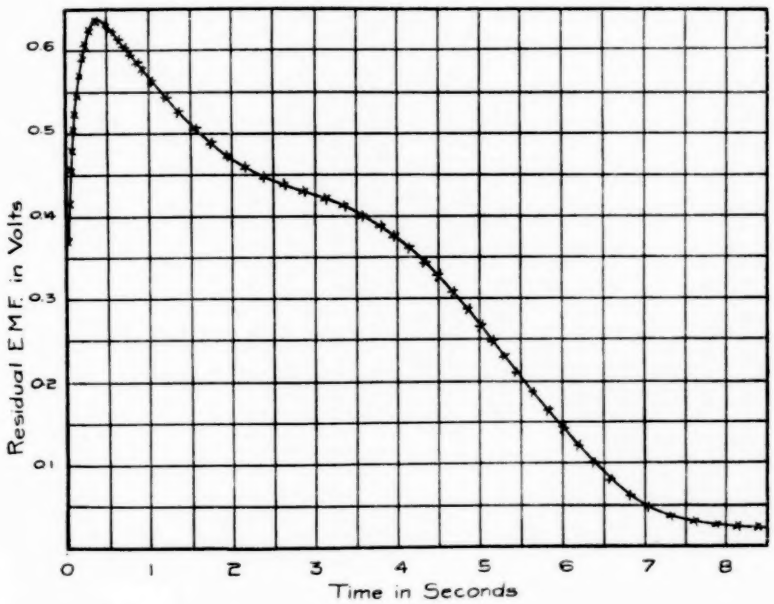


Fig. 2.

entirely to what happens during the first hundredth of a second after the interruption of the arc. If there have been any other measurements of the quantities here presented, I should be glad to get a reference to them.

Thus far nothing has been said concerning the resistance of the cooling arc; but if the relation between the residual electromotive force, current, and resistance should be that expressed in Ohm's law, it would be an easy matter to construct a resistance — time

[1] Hotchkiss, Bull. Amer. Phys. Soc., Vol. 2, No. 2, 1901.

[2] Blondel, London Electrician, Vol. 39, p. 615; Comptes rendus, Vol. 125, p. 164.

curve in which the ordinates would be the ratios of the corresponding ordinates of the electromotive force and current curves (Figs. 2 and 3). When such a curve is constructed it is found that the resistance at the end of the first hundredth of a second after the break is about 800 ohms, then gradually increases reaching a value of 1,000 ohms in less than 0.2 of a second.

After this the curve rises rapidly, becoming asymptotic to a line parallel to the axis of ordinates. However, upon examining the

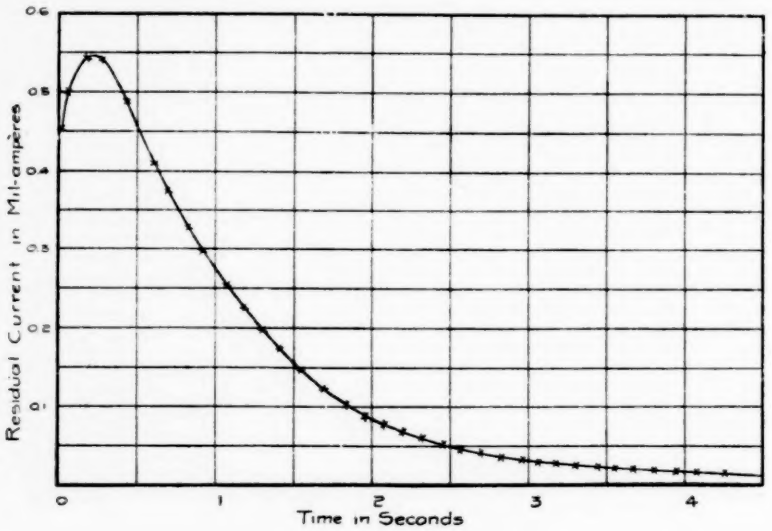


Fig. 3.

first part of this curve, remembering that the current was measured with a resistance of 1,000 ohms in the circuit in addition to the resistance of the arc, we find that the resistance of the arc *itself* during the first tenth of a second would be *negative* upon the assumption that Ohm's law expresses the relation between these quantities. We are thus forced to the conclusion that Ohm's law does not hold for the residual current.

## NOTE ADDED APRIL 25.

It is possible that an explanation of this phenomenon, in terms of the ionic hypothesis, may be built upon the following facts: first, the carbons of the electric arc are incandescent, and the tem-

perature of the positive terminal is nearly 1000° C. higher than that of the negative terminal; secondly, incandescent carbon is especially efficient in the emission of negative corpuscles, as illustrated in the well-known Edison effect, the rate of production increasing with the degree of incandescence. Then as long as the arc is in operation, the negative ions (emitted in far greater numbers from the incandescent tip of the positive carbon then from that of the negative carbon) are borne not across the arc-gap, but against the electric field back into the positive terminal from which they proceeded. But when the arc is interrupted the conditions are changed. There is no longer an impressed electric field to hold back the

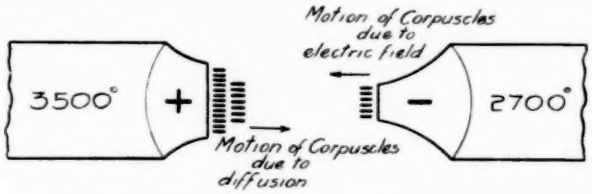


Fig. 4.

stream of corpuscles. They are freely emitted from both incandescent terminals (yet more abundantly from the positive) and diffuse across the arc-gap, this state of affairs continuing until the carbons have so far cooled down that the rate of production of the negative ions by the positive carbon is no longer in excess of the rate of their production by the negative carbon. (See Fig. 4.)

With this understanding of the matter it is easy to see why the arc requires a considerable time to reach a state of equilibrium; for this steady state would depend upon a constant difference of temperature between the electrodes, and this could only exist when each terminal had reached its maximum temperature and was so maintained.

The fact that graphite terminals give a small residual effect may be due to the fact that graphite is a fairly good conductor of heat (as ordinary carbon is not) and would thus tend to equalize the temperatures of the electrodes much more readily than ordinary carbons.

As to the maximum which occurs in the curves of both the

electromotive force and current (Figs. 2 and 3), it possibly may be due to the very appreciable time required for these ions to traverse the arc-gap; and if this is the case, the time at which the maximum occurs after the interruption of the arc may prove a useful factor in the determination of the ionic velocities.

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# SOME PHYSICAL PROPERTIES OF CURRENT-BEARING MATTER. — III. BOILING POINT.

By Paul R. Heyl.

THIS article contains a description of some experiments on the effect of a current on the boiling point of mercury and of two electrolytes, copper sulphate solution and dilute acetic acid. The results are all negative. The boiling point of mercury is not altered by 0.04° by a current density of over 100 amperes per square centimeter, and the electrolytes showed no change as great as 0.001° for current densities of 0.05 with the copper sulphate and 0.001 with the acetic acid.

## Mercury.

The general plan of the experiments on mercury was to boil the substance in two vessels, in one of which a current could be turned on at will, and to measure the difference of temperatures by a differential thermocouple. To form the latter a piece of platinum wire about thirty centimeters long was soldered at its ends, by means of zinc, to long pieces of copper wire. Zinc was chosen as the solder because its melting point is above the boiling point of mercury. The two junctions were protected by pieces of drawn out glass tubing and immersed in the vessels of boiling mercury, while the ends of the copper wires were connected to a galvanometer with a key in the circuit. The thermoelectric power of a copper-platinum junction at the temperature of boiling mercury is about ten microvolts per degree, according to Tait's diagram, and the galvanometer (of the Rowland wall pattern) gave a deflection of half a scale division per microvolt, consequently each scale division represented a difference of temperature of one fifth of a degree.

The only difficulty in the carrying out of this plan was to bring about the introduction of a rather heavy current into the boiling mercury without the formation of an arc. This was finally done by introducing the current into portions of the mercury which never rose to the boiling point. Fig. 1 shows the arrangement of the apparatus. A glass *T*-tube about one centimeter in diameter had one arm drawn out and connected by rubber tubing to a small glass funnel. The horizontal arm of the *T*-tube was closed by a small cork through which passed an iron wire *C* and a small glass tube *D*. Mercury was poured into the funnel until it half filled the horizontal arm and an iron wire *B* was inserted into the

mercury in the funnel. By the wires $B$ and $C$ connections were made through a switch, a rheostat and an ammeter to a dynamo. In the vertical arm of the $T$-tube was placed one of the copper-platinum junctions in its protecting tube, the end reaching down into the narrow part $A$. The joint at $E$ was open. The mercury was boiled at $A$ by applying a very small Bunsen flame, the vapor of mercury being drawn off through the tube $D$ by an aspirator, air entering freely at $E$ to prevent reduction of pressure. In addition, the tube $D$ was made to fit loosely in its cork that air might enter there also if necessary. The cross section of the mercury at $A$ was about 0.1 square centimeter, which of course was somewhat reduced by bubbles on boiling. The current was 10 amperes, making a current density of over 100 amperes per square centimeter at the point where the boiling took place. Higher than this one could not go without danger of forming an arc at $A$.

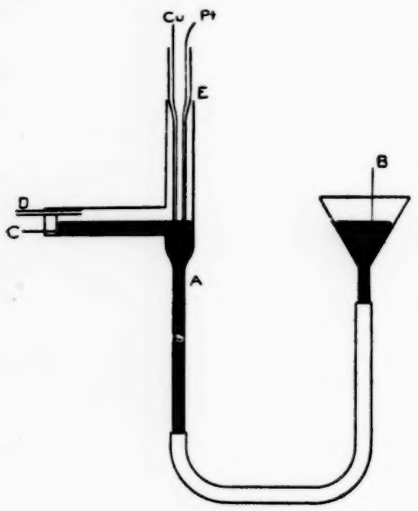

Fig. 1.

The second copper-platinum junction dipped into boiling mercury in a vessel which presented no features of interest. As in Fig. 1 mercury vapor was removed by an aspirator and a constant level was maintained by a funnel-shaped reservoir.

The mercury in both vessels being brought to boiling (with no current flowing) the galvanometer circuit was closed. It proved impossible to keep the instrument at zero, the reading varying slowly and irregularly several scale divisions on either side of the zero point. However, there were times when the reading remained stationary at or very near the zero point for several seconds, and by taking advantage of these periods it was possible to make a number of conclusive tests, throwing the current on, maintaining it for several seconds, and interrupting it without altering the reading. A change of one fifth of a scale division would have been easy to recognize, and this would have meant a change in the boiling point of 0.04°.

## ELECTROLYTES.

On account of the relatively high resistance of electrolytes one must be content with lower values of the current density and make up for this by more delicate measurements of change of temperature.

The first solution used was copper sulphate, of density 1.12. It is impossible to boil this in glass without some slight bumping, but in copper vessels it boils freely and steadily, and the boiling point may be taken by a Beckmann thermometer to 0.001°.

The first plan was to use a copper beaker as one electrode, dipping another electrode of copper rod into the center of the solution. The thermometer was dipped into the solution half way between the central electrode and the wall of the beaker. On applying to the boiling liquid a current whose average density was one fifth of an ampere per square centimeter there was a decided change in the reading of the thermometer which seemed to depend on the direction of the current. When the current was passed so that copper (and hydrogen) appeared at the inner surface of the beaker the thermometer rose at once, sometimes by as much as two or three tenths of a degree. With the current reversed the effect was usually a much smaller rise, sometimes preceded and sometimes followed by a slight fall. Bearing in mind the effect produced on the boiling point of a liquid by the nature of the surface of the containing vessel it seemed possible that the rapid deposition or removal of copper at the surface from which the steam bubbles took their rise might have been causing the irregular effect noticed. This suspicion was intensified when the thermometer showed no change as great as 0.001° on applying an alternating current of a frequency of 1,800 per minute and a density of 0.07 to the boiling solution.

Five different forms of apparatus were devised in the hope of eliminating the supposed effect of the changing surface before it was discovered that the trouble was due to something entirely different, namely the torrent of gas bubbles that arose from the electrodes. The electrodes, surrounded by a sheath of gas, were undoubtedly warmer than the solution, as in the water pail electric forge, and the bubbles, coming off in torrents, did not cool off completely before striking the bulb of the thermometer.

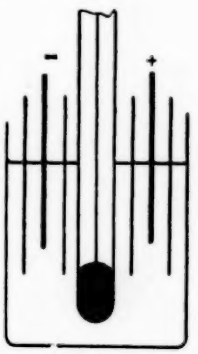

Fig. 2.

In Fig. 2 is shown a form of apparatus which can be used both to demonstrate the source of trouble and to eliminate its effects. The containing vessel is of copper varnished within with shellac. The Beckmann thermometer dips into the center of the liquid, and the current enters and leaves by two heavy copper rods, surrounded by wide glass tubes open at both ends. To reënforce the insulation of the copper beaker its walls were protected by sheets of mica, held in place between the walls of the beaker and the wide glass tubes. All the gas generated passes up the

glass chimneys without striking the thermometer, and it is possible to throw on and off the current in the boiling liquid without altering the reading of the thermometer by 0.001°. Of course there were times when the reading fluctuated slightly when there was no current flowing, and the boiling point rose very slowly in the long run on account of the increasing concentration of the solution. As in the experiments with mercury, advantage had to be taken of those times when the thermometer was quiescent.

To test still further the correctness of this diagnosis of the trouble a thermometer was inserted in one of the wide glass tubes. On applying a current to the boiling liquid this thermometer rose promptly about three quarters of a degree and fell again when the current was stopped, while the Beckmann thermometer outside was unaffected. In addition the wide glass tubes were removed and the Beckmann thermometer raised to the level of the electrodes. On turning on the current the thermometer rose at once.

The current density employed in these experiments was about 0.05 ampere per square centimeter in the neighborhood of the thermometer bulb.

Experiments were also made on a five per cent. solution of acetic acid, using carbon electrodes with a form of apparatus otherwise the same as that shown in Fig. 2. On account of the high resistance of this solution the greatest current density that could be attained was 0.001 ampere per square centimeter, and no change as great as 0.001° could be detected in the boiling point.

# ON THE VARIATION OF A CAPACITY WITH TEMPERATURE.

By Earle M. Terry.

THE measurements of small changes of capacity due to changes of temperature has been made possible by the use of the alternating current galvanometer. The following is a brief description of a modification of the instrument first used by Stroud and Oates.[1]

It is essentially of the D'Arsonval type, except that the field is built up of laminations of soft iron, and wound so as to be used directly on the 110-volt, 60-cycle, A. C. circuit. In the particular instrument used the laminations are circular disks about 30 cm. in diameter, and built up so as to have a cross-section about 4 cm. square. An opening about 1.5 cm. wide was made to admit the coil, the pale faces being tapered down to about 1 cm. in width.

The coil is made of no. 40 double insulated wire wound on a wooden form, and has a resistance of approximately 350 ohms, and coefficient of self-induction of 50 millihenries.

The great difficulty in manipulating the instrument is due to the fact that a closed coil suspended in an alternating magnetic field takes up a position of great stability, such that its axis is at right angles to the field, or so that the coil itself will include a minimum number of lines of force.

Since in any use of the instrument the coil must necessarily be closed through a greater or a less resistance, this stability reduces the sensibility enormously. Stroud and Oates overcame this difficulty by winding the coil upon a broad copper frame, in which the foucault currents induced in the sides acted like a closed coil placed at right angles to the galvanometer coil. This effect was made to predominate so that the coil, when on open circuit, took up a position so as to include a maximum number of lines of force, and was then brought back to zero by shunting with a suitable resistance.

[1] Phil. Mag., Dec., 1903.

The chief objection to this method of control is that it necessarily limits the range for which the instrument is sensitive. For if the external circuit includes capacity, the leading current produced by this in the coil will have the same effect as the torque on the sides of the frame, necessitating so small a shunt resistance as to greatly reduce the sensibility, as well as cause an annoying drift in the zero.

This action can probably be best explained by reference to a vector diagram, Fig. 1.

If $OA$ represents the flux in the field, then the vector $OB$ would represent the current induced by it in the galvanometer coil, providing it had no inductance, but simply resistance. There would then be no force acting upon the coil, for the product of two vectors at right angles is zero. Since, however, the coil possesses inductance, the current lags behind $OB$ and may be represented by a vector such as $OC$. The component $OD$ of this vector being 180° behind $OA$ gives the repulsion producing the objectionable stability.

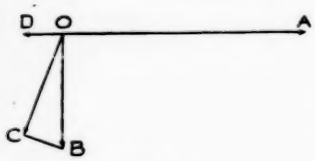

Fig. 1.

If a capacity be placed across the coil sufficient to swing $OC$ ahead until it has the direction $OB$, then the conditions of maximum sensibility is reached. If, however, the capacity be still further increased, so that the current has a component in the direction $OA$, then there will be an attraction and the coil will swing around so as to include a maximum number of lines of force.

The author has made use of this fact as a method of control and the manipulation of the instrument then becomes very simple. It is connected up the same as an ordinary galvanometer, except that no key should be placed in the galvanometer circuit, as the position of the coil depends upon the external circuit. If the set up contains both inductance and capacity, these will serve as part of the control, it being only necessary to shunt across the galvanometer coil with sufficient conductivity or capacity, as the case may be, to bring the galvanometer to a suitable zero point and sensibility.

One of the first uses to which the instrument was put in the laboratory at Madison was the measurement of an inductance by

Anderson's modification of Maxwell's method. Since the set up here contains both inductance and capacity, it was found that the capacity could be adjusted so as to make the galvanometer sufficiently sensitive and no control whatever was needed.

As it was necessary to first obtain a steady current balance, a double throw switch was placed in both the galvanometer field and the battery circuits, so that when rocked one way the instrument could be used to obtain the direct current balance, and when rocked the other way, to obtain the balance for the variable state.

In a set of five determinations made in this way, keeping the capacity constant and varying the resistances, the outstanding difference was 2 parts in 20,000 or .01 per cent. The precision of

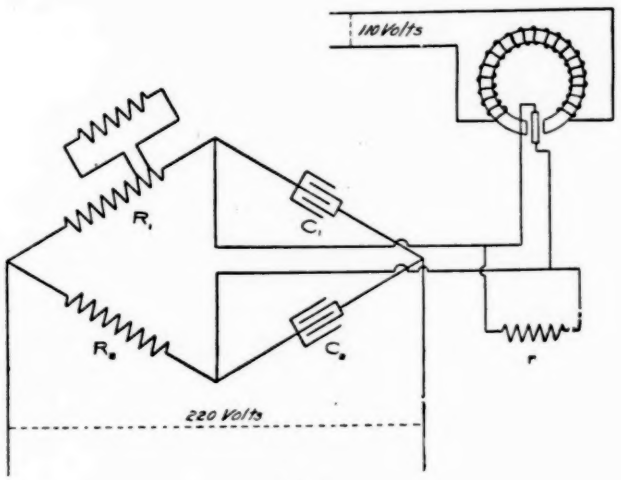


Fig. 2.

setting, however, was much closer than this, but the resistances could not be depended upon to a closer degree of accuracy.

It was found that no such agreement in results could be obtained on different days, which lead to the suspicion that the capacity must have an appreciable temperature coefficient.

In order to determine this, the bridge method for comparing capacities was used. The apparatus was arranged as shown in Fig. 2. The two capacities were subdivided condensers manufactured by Elliott Bros., having a range from .05 to 1 microfarad. The

one labelled $C_1$ was but recently purchased and was used as the standard, while $C_2$ has been in use for several years, and is the one for which the temperature coefficient was determined.

Both capacities were placed in tin boxes immersed in large water baths. $C_1$ was held at a constant temperature, while $C_2$ was varied between 17° C. and 33° C. The water in tank no. 2 was kept constantly stirred by two turbines driven by a water motor, while the temperature could be held at any point by means of a thermostat to .1° C. for any desired length of time. Owing to the large thermal capacity of the condenser it usually took about 48 hours for it to come to a uniform temperature throughout. This condition could of course be detected from the constancy of the capacity.

The resistances were new boxes manufactured by Otto Wolff, and could be relied upon to .01 per cent. In order to obtain a sufficiently fine adjustment a small portion of one of the boxes was shunted by a variable resistance, always large.

All connections were made of no. 12 heavily insulated copper wire.

An alternating pressure of 220 volts was applied to the bridge, while the galvanometer field was excited by 110 volts from half the secondary of the same transformer. Inasmuch as the capacity across the galvonometer coil was comparatively large the conductivity in the bridge being always small, it was found necessary in all cases to shunt across the galvanometer with a resistance $r$.

The following table gives an idea of the precision with which two capacities may be compared by this method.

| $R_1$ | $R_2$ | $C_1$ | $C_2$ | $R_1$ | $R_2$ | $C_1$ | $C_2$ |
|---|---|---|---|---|---|---|---|
| 1,957.1 | 2,000 | .2 | .19571 | 1,927.9 | 1,970 | .2 | .19572 |
| 1,947.3 | 1,990 | .2 | .19571 | 1,918.0 | 1,960 | .2 | .19571 |
| 1,937.5 | 1,980 | .2 | .19571 | 1,908.3 | 1,950 | .2 | .19572 |

It will be noticed that the outstanding difference is about 1 part in 20,000 or .005 per cent., while for any particular setting, a change of 1 part in 100,000 could be easily detected.

The temperature coefficient of each subdivision of the capacity referred to was determined. The data for those parts showing the extreme variation is given in the table below.

| Condenser. | Temp. | $R_1$ | $R_2$ | $C_1$ | $C_2$ | Temp. Coeff. |
|---|---|---|---|---|---|---|
| *D* | 16 | 1,947.4 | 2,000 | .05 | .04868 | |
| | 24 | 1,945.5 | 2,000 | .05 | .04863 | |
| | 29.2 | 1,944.3 | 2,000 | .05 | .04861 | |
| | 33.3 | 1,943.1 | 2,000 | .05 | .04857 | −.00011 |
| *B* | 16 | 1,999.6 | 1,982 | .2 | .20180 | |
| | 24 | 1,998.2 | 1,986 | .2 | .20123 | |
| | 29.2 | 1,994.7 | 1,986 | .2 | .20088 | |
| | 33.3 | 1,991.6 | 1,986 | .2 | .20061 | −.00033 |

The temperature coefficients for the other parts of the capacity are between these values and are as follows: Capacity *A*, − .00018; *C*, − .00028; *E*, − .00013.

For convenience in plotting, all of the curves have been placed upon the same sheet. The ordinates at the left refer to curve *A*. For curves *B* and *C*, subtract .2815 and .2870. The ordinates at the right are for curve *D*. For curve *E*, add .00015 to these values.

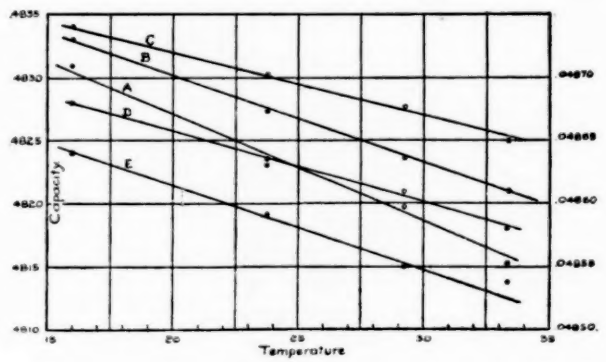


Fig. 3.

It will be noticed that all of the points lie reasonably close upon straight lines, with the exception of curve *E*. This condenser showed some leak, and it was impossible to obtain a perfect balance. The separate parts of the condenser taken as a standard were tested later and found to give values of the same order of magnitude.

In conclusion it would seem that a condenser has a temperature coefficient depending in value upon the construction, that it is negative, and of sufficient magnitude to require consideration when used in measurements of high precision.

PHYSICAL LABORATORY, UNIVERSITY OF WISCONSIN,
April 20, 1905.

# NEW BOOKS.

*Dynamics of Particles and of Rigid, Elastic, and Fluid Bodies.* By A. G. WEBSTER. Leipzig, B. G. Teubner, 1904. Pp. xii + 588.

As one reads the title page of this recent work on dynamics, one has a feeling of regret that no American publisher should have had the honor of producing it, and at the same time, one of pleasure that the work of an American professor should appear in this distinguished series of books being published by the house of Teubner. Before saying anything in review of the book, it may not be out of place to express here the pleasure it is to have a book with such clear type, excellent paper and binding. The whole mechanical execution of the work is excellent.

As Professor Webster notes in his preface, most books on dynamics treat the subject in a purely mathematical standpoint and the subdivisions are made accordingly. Within recent years, however, it has been recognized that the science belongs primarily to physics and that no student in the latter science can properly understand it unless he has a firm foundation in dynamics, so that "the aim of this book is to give in compact form a treatment of so much of this fundamental science of dynamics as should be familiar to every serious student of physics." The standard treatises on dynamics and the allied subjects of elasticity and hydrodynamics are so extended in their treatment that it is practically impossible for any physical student, whose main purpose in life is experimental research, to read them, except in part. With this thought in mind Professor Webster has prepared the book under review and has included in it what, in his opinion, constitutes the essential features of the subject and has added whatever sections were necessary in order to prepare the student to read other books more advanced or more detailed.

"The work divides itself naturally into three parts, the first of which considers the laws of motion in general and those methods which are applicable to systems of all sorts." The separate chapters of this part include "Kinematics of a Point," "Laws of Motion," "General Principles (such as that of Virtual Work)," "Work and Energy," "Principle of Least Action," "LaGrange's Equations," "Oscillations and Cyclic Motions."

The second part is devoted to the "Dynamics of Rigid Bodies," and is divided into two chapters, one dealing with "Systems of Vectors, Moments of Inertia, Centrifugal Forces, etc."; the other, with the "Dynamics of Rotating Bodies."

"The third part divides itself from the other two from the fact that in it the differential equations are partial, and in the others they are ordinary." As a preparation for this subject there is a full discussion of the theory of the potential function, which introduces the most important mathematical theorems and prepares for the subsequent chapters. Next follows the "Dynamics of Stress and Strain," the "Statics of Fluids," the "Problem of de St. Venant on the Flexion and Torsion of Prisms," and "Hydrodynamics." In this last chapter there are but 62 pages but there is a most satisfactory treatment of both irrotational and vortex motion, of wave motion, and of viscous fluids. At the end of the book there are five notes dealing with mathematical difficulties which have arisen in various chapters.

From this brief outline one may form an idea as to the scope of the work, but it may be of interest to call attention to certain features which distinguish it from any other book on the subject. Professor Webster has succeeded most admirably in preserving the perfection of analytical treatment called for in the development of the various theorems, and at the same time, he has presented in a most interesting manner the physical interpretation of the various formulæ. He has described, for example, some interesting modifications of Maxwell's dynamical top, and has called attention to certain practical illustrations of important theorems, such as are afforded by naval torpedoes, crushing mills, etc. Whenever in the course of a problem a formula appears which has a practical application, attention is called to this fact. In short, as a textbook of mathematical physics, in which both sciences claim an equal share, this book of Professor Webster's is by far the most interesting that is known to the writer of this review. What gives additional charm to the present treatise is the introduction into the text of personal notes dealing with the history of various theorems and experiments. In fact, the book as a whole, quite apart from the most important considerations, forms most delightful reading, owing to the charm of the language, the arrangement of the matter, the selection of illustrations and the thoroughly practical tendency of the treatment.

It is natural that different people should view dynamics from slightly different points of view, and should have their preference for certain modes of treatment. It seems to the reviewer that in places Professor Webster has sacrificed clearness of physical ideas for the sake of mathematical exactness. For instance, in speaking of Foucault's pendulum and gyroscope, sufficient emphasis is not placed upon the physical interpretation of the equations; and, in fact, most of the phenomena could have been deduced from most elementary considerations. A more elementary discussion of flexure and torsion might well have been added. The proofs of the important mathematical theorems such as those of

Stokes, Gauss, etc., are all given in a satisfactory manner, although, personally, in some cases the reviewer prefers others. In all cases, however, the illustrations chosen are most admirable.

From time to time in reading the book one meets certain sections which from one cause or another are not perfectly satisfactory, and to which it may be only fair to call attention. For instance, in discussing small oscillations a most ingenious method is adopted for the determination of the nature of the roots of Lagrange's determinant. The proof as given certainly requires amplification by the discussion of the reality of the variables at the very beginning of the argument. In this same connection, when the final solution for the oscillations is given, the phases of the partial vibrations are all made equal without any statement as to the reason for it, other than one that if the solutions be substituted in the differential equations they will be satisfied. (This same somewhat summary mode of treatment is given also in Rayleigh's Theory of Sound.) Again, in the discussion of zonal harmonics and in an illustration of their application to the attraction of a homogeneous body symmetrical about an axis of revolution, a solution of the problem is written which certainly is *a* solution. It would seem to be necessary for the completion of the argument to prove that it is the only solution. In fact, however, in no book on mathematical physics known to the reviewer is there any attention called to the necessity for this addition to the proof of this or similar formulæ, and it may, therefore, be that the need of such an addition is simply a prejudice of his. In the treatment of stress and strain the value of the ratio of expansion due to the strain is given in its usual determinate form, but is deduced simply for the case of a *pure* strain, whereas, the same formula is used in the following pages for other strains which are not pure. A more general proof of the expansion formula might have been given equally as well.

In deducing the formula for the work done in producing strains it would be better to emphasize particularly the fact that the formula deduced is for a *change* in an existing strain. Again, in writing the formulæ for a simple shear as an illustration of equilibrium on page 461, it would have been better to have followed the same definition as on page 440 and thus to have avoided confusion.

These points of criticism are of minor importance obviously, for the general plan of the book is so good, the omissions are so few, the mathematical treatment is so clear and elegant, the physical illustrations are so well chosen, that this treatise is by far the best suited of all books known to the reviewer to be placed in the hands of physical students either in universities or in the higher grades of technical schools.

J. S. Ames.

*The Becquerel Rays and the Properties of Radium.* By Hon. R. J. STRUTT. 8vo, pp. vii + 214. London, Edward Arnold, 1904.

*Radioactivity: An Elementary Treatise from the Standpoint of the Disintegration Theory.* By FREDK. SODDY. 8vo, pp. xi + 214. London, The Electrician Publishing Co., 1904.

*Radioactivity.* By E. RUTHERFORD. 8vo, pp. ix + 399. Cambridge, The University Press, 1904.

*Untersuchungen über die Radioactiven Substanzen.* By MME. S. CURIE. Translated into German by W. KAUFMANN. 8vo, pp. viii + 132. Braunschweig, Vieweg und Sohn, 1904.

*Das Radium: Seine Darstellung und seine Eigenschaften.* By JAQUES DANNE. 8vo, pp. 84. Leipzig, Veit & Co., 1904.

When we remember the almost unprecedented popular interest that has been aroused by the discoveries in the field of radioactivity it is a pleasant surprise to note how few sensational books have appeared on the subject. It is true that a few pamphlets of an objectionable character, and numerous newspaper articles, have been published. But the books on radioactivity are almost without exception of permanent scientific value. The scientific public also is to be congratulated on the fact that the authors of these books are usually themselves workers in this most interesting and difficult field, who speak of what they know at first hand, and to whose investigations the rapid development of the subject is in large part due.

None of the books here considered can be said to give a "popular" account of radioactivity, if by this is meant a treatment that would be intelligible to one with no knowledge of physics. In fact an account of this subject intended for one entirely ignorant of physics would have to be too superficial to be of much value. But for one who already has some knowledge of fundamental laws and principles and who wishes something more than can be obtained in the popular magazines, the admirable book of Strutt on "The Becquerel Rays and the Properties of Radium" will be found in the highest degree interesting and instructive.

Starting out with a chapter on the electric discharge in high vacua, — introduced in order to familiarize the reader with the cathode rays, the canal rays, and related matters, — the author develops the subject of radioactivity in a manner which is at the same time historical and logical. The book is written in an interesting and pleasing style. It is entirely free from mathematical methods, but rigorous and sound; written in a conservative spirit quite free from any suggestion of sensationalism, while at the same time doing full justice to the remarkable and intensely interesting features of the subject. Appendixes describe several simple experiments for illustrating the properties of radioactive sub-

stances; the theory of the deflection experiments with the $\beta$-rays; and a brief account of the methods of extracting radium from pitchblende. In its clearness and soundness as well as in its interesting style Mr. Strutt's book recalls the writing of Tyndal. It may be strongly recommended not only to the general readers for whom the author seems to have intended it, but also to scientific workers who have not found time to follow the extensive and somewhat confusing literature of radioactivity and now feel the need of a book that shall present the main facts, and their bearing upon scientific theories, with clearness and reasonable brevity. The fact that Mr. Strutt's book is the most recent of those here considered is also of some importance.

Those who wish to obtain a somewhat more detailed knowledge of the methods and results of the study of radioactivity, yet without making an extended study of the subject, will turn to Soddy's "Elementary Treatise on Radioactivity from the standpoint of the Disintegration Theory," the material of which first appeared as a series of articles in the London Electrician beginning in October 1903, and has since been suitably revised and expanded. The book is clearly written and has doubtless proven very generally useful. It has the disadvantage, in some accounts perhaps the advantage, of occupying an intermediate position among the books here considered; it contains so much that is beyond the experience of the general reader, that it cannot well serve as a popular account of the subject; while for those who wish to make a somewhat serious study of radioactivity the treatment is not sufficient in detail. The discussion of the significance of the various phenomena of radioactivity in their bearing upon physical theories is both interesting and suggestive. Especially is this true in the case of the last chapter—"Anticipations." The author's temerity in introducing a chapter of this kind is in part justified by recent developments, for in several instances the views advanced have been either wholly or in part confirmed.

It need hardly be said that the standard treatise on radioactivity is that of Rutherford; and it will doubtless remain so as long as the work is frequently revised so as to keep up with the rapid development of the subject. There are some perhaps, who would prefer to have a treatise of this kind so written as to be independent of any particular theory of the phenomena considered. But when we recall the prominent part taken by Rutherford in the development of the disintegration theory of radioactivity, we can scarcely expect a treatment of the subject in which this theory remains in the background; for, since the first and almost prophetic suggestion of Elster and Geitel, no one has done so much as he to develop the theory and to bring about its almost universal acceptance. Scarcely an example occurs to me of a theory that has been so altogether useful as this. It has not only been of immense assistance in guiding

investigation, having led to the discovery of phenomena and laws which would otherwise have remained unsuspected, but its aid in the statement of phenomena has become almost indispensable. A writer who should attempt to give an account of the complicated phenomena of radio-activity now known, without the assistance of the concrete pictures furnished by the disintegration theory, would find that he had on his hands a very difficult undertaking. The author says in this connection: "The phenomena exhibited by the radio-active bodies are extremely complicated, and some form of theory is essential in order to connect in an intelligible manner the mass of experimental facts that have now been accumulated. I have found the theory that the atoms of the radio-active bodies are undergoing spontaneous disintegration, extremely serviceable not only in correlating the known phenomena, but also in suggesting new lines of research. The interpretation of the results has, to a large extent been based on the disintegration theory, and the logical deductions to be drawn from the application of the theory to radio-active phenomena have also been considered." Professor Rutherford's treatise will be consulted by those who seek a thorough and detailed account of methods and results in the field of radioactivity; by those who wish to find references to original articles in this field, for the citations to the literature of the subject are wellnigh complete; by those wishing an authoritative account of the development and present status of the disintegration theory; in fact by every one who has need of a *treatise* on radioactivity, rather than a popular or semi-popular account. Special reference should be made to the very useful chapters on the "Ionization Theory of Gases" and "Methods of Measurement." Strange to say no other book with which I am acquainted contains a really usable account of the experimental methods used in the study of radioactivity.

The three books thus far considered, while differing widely in other respects, have one feature in common: the phenomena are interpreted in each case from the standpoint of the disintegration theory. All three books represent the British school of radioactivity, if we may use the term. In the earlier books by Madame Curie and by Danne we have the French school represented. Madame Curie's book will always have a peculiar interest of its own, which will persist even after the subject has progressed to such an extent that the value of the book is chiefly historical. That time, however, has not yet come. Madame Curie's account of the work that led to the discovery of radium, and of the properties of radioactive substances, will still be found not only interesting but instructive. The experimental results are stated, usually in a brief style, without any attempt at interpretation and without preference for any theory. The disintegration theory has been of immense value in the study of radioactivity, and doubtless represents the nearest approach to

the truth that has yet been reached. Nevertheless to consider the phenomena at times simply as phenomena and not in the light of any theory, is very useful, and will help to prevent one from falling into a rut. It is interesting also to see the subject in the different perspective which results from taking the French rather than the British viewpoint.

The little book by Danne, entitled "Radium, its Preparation and Properties," goes into the chemical side of radio-activity, especially in the case of the extraction of radium from its ores, more fully than any other book with which I am familiar. The discussion of the physical properties of radium, however, although clearly presented, is much briefer and less complete than that contained in the books already mentioned.

The minor part played by the chemical side of radioactivity in the books here considered is significant and calls attention to an unfortunate condition of affairs, which, unless it is remedied, will seriously retard further progress in this most important field. The study of radioactivity thus far has been almost wholly from the physical side, and in the great majority of cases has been carried on by physicists; the chemistry of the radioactive elements and their compounds, and the chemical aspects of radioactivity in general, have scarcely been studied at all. The development of the processes used in the extraction of radium from its ores and the discovery of the evolution of helium form almost the only exceptions to this statement. The excuse usually urged for this condition of things, namely the rarity and expense of the more strongly active substances, does not seem to me a good one. It is true that the rarity of radium prevents the employment of ordinary chemical procedure in its study. But new conditions require new methods. If Madame Curie had adhered solely to the methods of orthodox chemistry the new element would not have been discovered. It appears to me that the subject of radioactivity has reached a point where further progress will be slow unless aided by the effective coöperation of both physics and chemistry.

In none of the books here considered are the experiments with radioactive substances in the fields of medicine and biology adequately treated.

ERNEST MERRITT.

*Handbuch der Spectroscopie, Band III.* By H. KAYSER. S. Hirzel, Leipzig, 1905. Pp. viii + 604.

The third volume of Kayser's Handbook of Spectroscopy fulfills the promise of the earlier volumes as regards completeness and thoroughness of treatment. The present volume deals exclusively with absorption spectra and includes not only all that has been amassed by an army of investigators concerning the selective absorption of the visible rays but

likewise all that has thus far been learned by the use of photographic methods concerning absorption in the ultra-violet spectrum and by means of the thermopile, bolometer and radiometer concerning absorption in the infra-red. Unfortunately the extensive explorations of the infra-red spectrum made by W. W. Coblentz were not completed in time to be included as a whole in Professor Kayser's Compendium, but his results in so far as they had appeared up to the middle of the year 1904 are included.

Chapter I. of the present volume deals with the apparatus and methods for the study of absorption and Chapter II. with variations in absorption spectra and the influence of temperature, pressure, etc., upon the same. Chapter III. which was written by Professor Hartley of Dublin, deals at great length with the difficult question of the relations between the absorbing power and constitution of organic compounds. The remainder of the volume consists of a systematic summary of the absorption of the various elements and their compounds with an alphabetical descriptive list of all known absorption spectra together with references to the original sources from which the data have been derived. E. L. N.

*Modern Theory of Physical Phenomena.* By AUGUSTO RIGHI. Translated by AUGUSTUS TROWBRIDGE. 8vo, pp. ix + 165. New York, The Macmillan Co., 1904.

The eight years that have elapsed since the introduction of the electron into physical theories have witnessed changes of a most fundamental and far reaching character in our manner of interpreting physical phenomena. While it is to the study of the cathode rays that we owe the first experimental evidence of the existence of charged particles smaller than atoms, the utility of the electron in physical theory has not been confined to the phenomena of the discharge in gases, nor even to the discussion of phenomena of a purely electrical character. There is now not a department of physics left in which the modern conception of electrons has not played a part. In some cases it has led to new theories; in others it has made possible the statement of old theories in new and more concrete form. For one who wishes to remain in touch with the rapid developments of physics a knowledge of the fundamental notions of the modern electron theory is therefore absolutely essential.

It is the purpose of Professor Righi's excellent book to give this knowledge of the fundamental notions. The book is non-mathematical; only rarely does an algebraic or geometrical discussion appear in a footnote, and always of the simplest character. Beginning with a consideration of ordinary electrolysis the author then considers the Zeeman effect, cathode rays, conduction in gases and solids, radioactivity, and finally the consti-

tution of matter. The treatment is brief, but remarkably clear. In so small a book no detailed discussion of the many topics treated can be expected. But the outline is given, and with it and the suggestion that there is more to the subject than is contained in this book. References to original articles are frequent. The translation from the Italian, undertaken by Professor Trowbridge with the coöperation of the author, is highly satisfactory.

Although Professor Righi himself has carried out numerous important investigations along lines closely related to electron theory, it cannot be said that much of the work leading to the development of this subject has been done in Italy. In the opinion of the reviewer this fact adds to the value of a book like that here considered. The subject is presented to us by one who sees it from the outside. The treatment is appreciative, but at the same time conservative; and there is none of the faulty perspective, resulting from unrestrained enthusiasm, which is sometimes seen in similar books by English authors.

ERNEST MERRIT.

*The Recent Development of Physical Science.* By WILLIAM CECIL DAMPIER WHETHAM. 8vo, pp. xii + 344. Philadelphia, P. Blackiston's Son and Co., 1904.

In modern scientific investigation coöperation between different related branches of science is becoming more and more essential. Each investigator is a member of the great scientific army that is battling with the unknown. In modern warfare individual companies and regiments do not fight alone, but each part of the army keeps itself informed of the progress made by the rest, so that an advantage gained by one may be utilized by all.

It is the recognition of this need of scientific coöperation that has led to the preparation of Mr. Whetham's book. The author says: "Thus it happens that an acquaintance with the knowledge newly acquired in one department of science is necessary for the study of another; indeed, the phenomena which need for their interpretation the methods of two branches of science have proved often the most fruitful field of inquiry. For reasons such as these it has been thought possible that a short account of some of the important investigations now being carried on in the physical laboratories of the world might be useful to students of science in general; while it is hoped that, by treating the subjects as far as possible without technical language, the book may also appeal to those who, with little definite scientific training, are interested in the more important conclusions of scientific thought."

It will be seen that the general purpose of the book is the same as that

of Righi's "Modern Theory of Physical Phenomena." But while the latter book deals only with the various phases of the electron theory, the former covers a far wider field. The scope of the book is indicated by the following list of topics treated: The Philosophical Basis of Physical Science; The Liquefaction of Gases and the Absolute Zero of Temperature; Fusion and Solidification; The Problems of Solution; The Conduction of Electricity through Gases; Radioactivity; Atoms and Ether; Astrophysics.

The attempt to cover so much ground unfortunately results in a less thorough treatment of the topics considered than that of Righi. References to original sources are absent. Occasionally the statements made are misleading, either because of their brevity or actual inaccuracy. Take for example the interpretation put upon the negative Joule-Thomson effect in hydrogen, which the author ascribes to a force of repulsion between the hydrogen molecules. Later the reversal of the effect at —80° C. is mentioned, and will naturally be interpreted by the reader as indicating a change at that temperature from molecular repulsion to molecular attraction. One who is prepared to read the chapter on the liquefaction of gases understandingly will not look with favor upon a theory that requires such an assumption as this, — an assumption that was perhaps natural enough fifty years ago, but which is now no longer necessary.

A misleading statement of another kind appears in the chapter on conduction through gases, where the author says that "the effect of very high vacua on the electric discharge was first systematically investigated by Sir William Crookes." To those who are familiar with the classical articles of Hittorf, whose publication preceded the work of Crookes by several years, and which contain descriptions of phenomena that are even now being rediscovered, such a statement seems unfortunate.

In trying to make the same book serve for the two classes of readers referred to in the preface — namely the educated man who has a general interest in science, and the scientific worker in other fields, — the author has undertaken a very difficult task. In fact it appears to me almost impossible to carry out such an undertaking so that the result shall be satisfactory from both points of view. Some lack of exactness is inavoidable in a popular account of scientific work, and even a certain amount of carelessness in statement is excusable, although regrettable. But in a book intended for workers in other branches of science — men who have scientific training and the scientific instinct, but whose work has simply been along other lines — any carelessness in the presentation of what is to the reader a novel theory is apt to diminish the value of the book very greatly. It must be remembered that many hypotheses or modes of thought to which the physicist has become accustomed may appear in an entirely different light to workers in other fields. A book written for

such an audience has failed in its purpose unless it gives to its readers an understanding of the reasons which have led to the adoption of new hypotheses.

In some cases I think that Mr. Whetham's book has failed in just this way. Consider for example the hypothesis that lies at the foundation of all branches of the electron theory — the assumption of the existence of portions of matter smaller than atoms. This assumption is introduced in the chapter on conduction through gases in an off hand way, natural perhaps to one long familiar with the, at first, startling suggestion. Later there is indeed an attempt to give the reasons for believing that corpuscles are smaller than atoms. But the discussion appears to me entirely inadequate. It really makes the whole argument rest on the results of J. J. Thomson's determination of the charge carried by an ion in air. The results of these experiments are certainly interesting, and are important when taken in connection with the great mass of indirect evidence pointing in the same direction. But when one remembers the number of questionable assumptions that are involved in the determination, no one would be willing to accept the conclusion on such evidence alone. Certainly the chemist, who sees in the electron hypothesis a contradiction of laws which he has long regarded as fundamental, will not be converted to the new theory by such a presentation of the case. To make the book of value to such readers the author should have borne in mind the skeptical attitude held by most physicists only a few years ago, and should have indicated the steps by which accumulating experimental evidence virtually forced the acceptance of the electron theory.

There are numerous instances where criticism similar to that above might properly apply. The reviewer feels that the author has had the opportunity to supply a book whose need is strongly felt; but that the opportunity has not been fully utilized. The book is written in an interesting style, however, and contains much that it would be difficult to find in better form elsewhere. The essential fault that one finds in the book is not that it is bad, but that, although good, it might have been so much better.

ERNEST MERRITT.